California Regional Water Quality Control Board
Santa Ana Region

October 26, 2001

ITEM: 8

SUBJECT: **TOXICS TOTAL MAXIMUM DAILY LOADS (TMDLS) FOR THE SAN DIEGO CREEK/NEWPORT BAY WATERSHED**

At the September 26, 2001, Board meeting, the Regional Board was informed of the process and timeline by which toxics total maximum daily loads (TMDLs) for San Diego Creek and Newport Bay are being developed. Board staff will report on the specifics of the selenium, diazinon, and chlorpyrifos TMDLs at this Board meeting. Copies of the draft TMDL reports are attached.

California Regional Water Quality Control Board
Santa Ana Region

Agenda Item: 8

Draft Selenium (Se)
Total Maximum Daily Load (TMDL)
for Newport Bay and San Diego Creek Watershed

October 26, 2001

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1. INTRODUCTION

Selenium (Se) is a natural trace element in the environment. It has chemical and physical properties that are intermediate between those of metals and non-metals. It is an essential nutrient for fish, birds, animals, and humans. However, excess amounts are found to cause toxicity. One of the most important features of selenium ecotoxicology is the very narrow margin between nutritionally optimal and potentially toxic dietary exposures for vertebrate animals (Wilber, 1980).

1.1. SELENIUM IN THE ENVIRONMENT

Selenium exists in different environmental compartments that are atmospheric, marine, and terrestrial in nature. Heterogeneity in its distribution results in movement of selenium among those compartments (Nriagu, 1989). Generally speaking, parent materials known to have the highest Se concentration are black shales (around 600 ppm) and phosphate rocks (1-300 ppm), both potentially giving rise to seleniferous soils and food chain Se toxicity. Selenium can become mobilized and concentrated by weathering and evaporation in the process of soil formation and alluvial fan deposition in arid and semiarid climates (Presser, 1994). Selenium contamination of aquatic ecosystems is of special concern in large parts of California, and other semi-arid regions of western North America (Seiler *et al.*, 1999).

1.2 CHEMICAL FORMS

The chemical speciation of Se is a critical consideration in assessing Se contamination in that the bioavailability and toxicity of selenium are greatly affected by its chemical forms. Selenium can occur in four different oxidation states: selenide (–2), elemental selenium (0), selenite (+4), and selenate (+6). In general, selenate (Se^{6+}) has a high solubility and is the most mobile in water. Selenite (Se^{4+}) is soluble in water but its strong affinity to be adsorbed to soil particles greatly reduces its mobility. Elemental Se (Se^{0}) exists in a crystalline form and is usually incorporated in soil particles. In most surface waters, selenate and selenite are the most common chemical forms. Selenite is the most bioavailable of the dissolved phase inorganic species (Maider *et al.*, 1993; Skorupa, 1998). Organo-selenide was also found to be very bioavailable and hence toxic to algae, invertebrates, and fish (Maider *et al.*, 1993).

Selenium is also found in particulate phases, which may include primary producers (*e.g.*, phytoplanton), bacteria, detritus, suspended inorganic material, and sediments. Interactions and transformation of selenium between dissolved and particulate phases could be biological, chemical, physical in nature. Those reactions play an important role in selenium toxicity (Luoma and Presser, 2000).

1.3. BIOACCUMULATION

Selenium tends to bioaccumulate in bio-tissues and causes toxicological effects. There is strong evidence that the major selenium uptake route into fish is not accumulation from water, but rather via the food chain (Fowler and Benayoun, 1976; Wilber, 1980; Luoma *et al*., 1992). Bioaccumulation of selenium in lower trophic level invertebrates (*e.g.*, zooplankton and bivalves) is a critical step in determining the effects of Se since higher trophic level predators such as fish and birds feed on invertebrates. Studies have shown that uptake of dissolved Se by invertebrates is not as important as uptake from diet (Luoma *et al.*, 1992; Lemly, 1993). Luoma and Presser (2000) suggested that direct uptake of particulate selenium by invertebrates via filter-feeding or deposit feeding is the primary route for selenium to enter the food web. In laboratory studies of the mussel *Mytilus edulis*, dissolved selenite (+4) is the most bioavailable form of inorganic Se taken up from solution (Wang *et al.*, 1996). Luoma *et al.* (1992) showed that the uptake rate of dissolved selenite explained less than 5% of the tissue concentrations of Se accumulated by the clam *Macoma balthica* at concentrations typical of the San Francisco Bay-Delta. The role of dissolved organic selenides in Se bioaccumulation is not as well understood as availability of inorganic Se, but it is unlikely that its uptake rate is greater than uptake rates from food (Luoma and Presser, 2000).

2. PROBLEM STATEMENT

2.1. GEOLOGICAL AND BIOLOGICAL SETTING

The Newport Bay/San Diego Creek (NB/SDC) watershed is located in Central Orange County in the southwest corner of the Santa Ana River Basin, about 3.5 miles south of Los Angeles and 70 miles north of San Diego. Newport Bay is a combination of two distinct water bodies - Lower and Upper Newport Bay, with areas of 752 and 1,000 acres, respectively. They are divided by the Pacific Coast Highway (PCH) Bridge. The Lower Bay, where the majority of commerce and recreational boating exists, is highly developed. The Upper Bay contains both a diverse mix of development in its lower reach and an undeveloped ecological reserve to the north.

Upper Newport Bay (UNB) is primarily an estuary with fresh water inflows from tributaries and drainage channels. It is home to six federally and state listed threatened and endangered species (five bird species and one plant species) and is designated as an Ecological Reserve by the State of California. The primary source of freshwater flowing into UNB is San Diego Creek. Mixing of fresh and salt water and the seasonal variability in salinity within the Bay promotes a variety of diverse estuarine habitats. The major tributary of San Diego Creek is Peters Canyon Channel, which includes Peters Canyon, Rattlesnake Canyon, and Hicks Canyon Washes that have their headwaters in the foothills of the Santa Ana Mountains. Above the junction with Peter Canyon Channel, San Diego Creek extends in an easterly direction to include Bee Canyon, Round Canyon, Agua Chino Wash, Borrego Canyon Wash and Serrano Creek, all of which have their headwaters in the foothills of the Santa Ana Mountains. Other fresh water inputs to the Bay include Santa Ana-Delhi Channel, Big Canyon and other local drainages. Table 2.1 summarizes the drainage areas of the tributaries of the Newport Bay watershed.

Table 2.1. Drainage Areas of the Newport Bay Watershed

Tributary	**Drainage Area** (acres)	**Drainage Area** (mile^2)
San Diego Creek	47,300	73.9
Peters Canyon Channel	28,200	44.1
Santa Ana-Delhi	11,000	17.2
Other Drainage Areas	12,000	18.8
Total	98,500	154.0

In the San Joaquin Valley in central California, Se contamination was reported to result from the dissolved mineral load drained from seleniferous marine sedimentary strata (Presser, 1994). The Irvine Subbasin in the SDC watershed and the Main Orange County Basin consist of thick sequences of alluvial, fluvial, and marine sediments deposited on Cretaceous igneous and metamorphic rocks (Camp Dresser & Mckee Inc., 1985). Therefore, geohydrological movement mechanisms of selenium similar to those in the San Joaquin Valley may be expected to occur in this watershed.

2.2. METHODOLOGY FOR ECOLOGICAL IMPACT ASSESSMENT

It is important to acquire multiple lines of evidence to assess the occurrence or absence of ecological impairment in an aquatic environment (Hall and Gidding, 2000). A protocol proposed by Lemly (1995) to assess aquatic hazards due to selenium requires Se concentration data in five ecosystem components – water, sediment, benthic macroinvertebrates, fish, and aquatic birds. The hazard assessment procedure focuses on food-chain bioaccumulation and reproductive impairment in fish and aquatic birds, which are considered to be the most sensitive biological end points for determining potential ecosystem-level impacts of selenium (Lemly, 1993). Incomplete data sets, with one or more ecosystem components missing, will weaken the predictive power of the assessment, but it can still be performed. In this report, field data on selenium are compiled and compared with levels of concern reported in the literature to assess the ecological impacts of selenium in the NB/SDC watershed.

2.3. DATA AVAILABLE FOR ANALYSIS

2.3.1. Surface and Groundwater

Irvine Ranch Water District (IRWD) was required under a NPDES permit for the Wetland Water Supply Project to monitor selenium concentrations and loading to the Newport Bay. Monthly monitoring was conducted at two locations in San Diego Creek (Michelson and Campus Drives) from December 1997 to March 1999.

Dr. Barry Hibbs' group at Cal State University Los Angeles conducted a study to identify sources of selenium within the San Diego Creek Watershed (Hibbs and Lee, 2000). Samples were collected from surface water channels and shallow groundwater basins from April 1999 to December 1999. Sampling occurred mostly in low flow conditions.

Dr. Fred Lee (G. Fred Lee & Associates), and Scott Taylor (Robert Bein, William Frost and Associates) recently completed an investigation of sources of acute toxicity in the San Diego Creek watershed (Lee and Taylor, 2001). Selenium is one of the chemicals monitored in the study. The study involved sampling during wet and dry weather at ten surface water locations within the watershed.

No recent water column data are available for selenium concentrations in the Bay. For the purposes of this report, historical water column concentrations in the Bay were extracted from EPA's STORET database.

2.3.2. Precipitation and Flow Data

Precipitation and flow data were obtained from OCPFRD as part of its monitoring program (OCPFRD, Hydrologic Data Report 1998-1999 Season). Precipitation data used in this report were collected at the Tustin - Irvine Ranch and Newport Beach Harbor Master stations. OCPFRD conducted an one-week investigation on nutrient sources in the San Diego Creek watershed, in which flow rates in tributaries were measured. The flow data are used in this report for load calculations and estimation of groundwater contribution to surface flow.

2.3.3. Sediment Data

Monitoring data for selenium concentrations in sediments are rare in recent years. In the past, selenium was monitored at locations in the Creek and the Bay. The historical data provide information regarding concentrations of Se in sediments. These data were extracted from EPA's STORET database. In 1995, a sediment chemistry analysis was performed as part of a dredging project in Upper Newport Bay, which was completed in 1999 (TOXSCAN, 1995). The sediment chemistry data are used to assess ecological impacts due to selenium.

2.3.4 Invertebrate Data

The State Mussel Watch Program (SMWP) is an annual monitoring program run by the State Water Resources Control Board in cooperation with the RWQCBs. California Department of Fish and Game staff perform the field and laboratory work. The Program monitors bioaccumulation of toxic chemicals in invertebrates and uses the monitoring results as indication of contamination levels of a wide variety of pollutants.

2.3.5 Fish Data

Initiated in 1976, the Toxic Substances Monitoring Program (TSMP) is an annual monitoring program, in which the presence of toxic substances in waters is determined by analyzing tissue from fish and other aquatic organisms. Like the SMWP, the field and laboratory work is conducted by the Department of Fish and Game on behalf of the State Board/Regional Boards.

2.4. IMPAIRMENT ASSESSMENT

In 2000, USEPA promulgated a rule "Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California" (California

Toxics Rule, May 18, 2000). The California Toxics Rule (CTR) sets numeric standards for selenium to protect aquatic systems from selenium toxicity. These standards are listed in Table 2.2. The CTR standards can be compared to water column concentrations for impairment assessment.

Table 2.2 USEPA Water Quality Standards for selenium in fresh and salt waters

	CCC[a] fresh water	CMC[b] Saltwater	CCC[a] Saltwater
Selenium	5.0[c]	290[d]	71[d]

[a]Criterion Continuous Concentration (4-day average)
[b]Criterion Maximum Concentration
[c]This criterion is expressed in the total recoverable form.
[d]The criteria are expressed in terms of the dissolved fraction in the water column.

There have been many laboratory and field studies for investigation of Se environmental chemistry and toxicology and the results are reported in the literature. Engberg *et al.* (1998) and Henderson *et al.* (1995) summarized selenium levels of concern in five environmental media (Table 2.3). The National Irrigation Water Quality Program (NIWQP) published a guidance document for background levels and levels of concern for biological effects due to a number of constituents in various environmental media (NIWQP, 1998). These reviews show that levels of concern fall in a fairly wide range for each environmental medium. In this report, the concentration levels listed in Table 2.3 are used to assess ecological impacts in NB/SDC watershed. It should be noted that the level of concern for water column concentrations of selenium is as low as 2 μg/L the US Fish & Wildlife Service that the CTR criterion be revised from 5 μg/L (total recoverable) to 2 μg/L (dissolved) (see Section 3.3).

Table 2.3. Selenium levels of concern for five environmental indicators (mg/kg, dry weight except as noted). (Engberg *et al*., 1998 and Henderson *et al*., 1995).

Indicator	**Normal background**	**Level of concern**	**Toxicological and reproductive effects a certainty**
Water (μg/L)	< 0.5-1.5	2-5	> 5
Sediment	< 2	2-4	> 4
Food chain	Usually < 2, Rarely > 5	3-7	> 7
Fish	Usually < 2, Rarely > 5	4-12	> 12
Avian eggs	Usually < 3, Max < 3	3-8	> 8

2.4.1. Concentrations in Waters

As reported in the Toxics Problem Statement for NB/SDC watershed (2001), selenium concentrations at Campus Drive in San Diego Creek consistently exceed the California Toxics Rule (CTR) criterion for fresh waters (5μg/L). Water column concentration data at Campus Drive in San Diego Creek are shown in Figure 2.1. The concentrations are well above the level that Engberg *et al* characterized as certain to cause toxicological and reproductive effects (see Table 2.3). This suggests that selenium is likely to cause ecological impacts in San Diego Creek.

2.4.2 Concentrations in Sediments

Very few recent data are available for selenium levels in sediment in the Creek and the Bay. Historical data (1976-1990, EPA STORET database) are used as an indication of contamination in sediments. Concentrations in sediment samples from San Diego Creek (Campus Drive) and the Santa Ana-Delhi channel range from 0.02 to 3 mg/kg dry weight (dw), of which 78% are below 1 mg/kg dw. Concentrations in the Bay sediment range from 0.02 to 4 mg/kg dw, with 75% below 1 mg/kg dw. These data suggest that impacts caused by sediment in the watershed during the sampling years were minimal when compared to the values for sediment in Table 2.3. However, it should be noted that the watershed has undergone significant changes since the years of the data. The data cannot be used to reflect the current Se levels.

As part of the 1995 dredging by OCPFRD, chemical analyses were performed on bulk sediments collected from Upper Newport Bay. Results show selenium concentrations were all below 1.0 mg/kg dw (ranging form 0.5 to 0.8) at the Unit 1 basin (approximate location) and access channels, with a detection limit of 0.1 mg/kg dw.

A more recent sampling and analysis of Bay sediment by Ogden Environmental and Energy Services was conducted in 1999 (Ogden, 2000). Results show that the amounts of selenium in sediment samples collected at four locations in Newport Bay (Lido Island, South Bay Front, Dover Shores, and Linda Island) were all below the detection limit of the analytical method used (1 mg/kg dw), suggesting minimal impacts due to sediment selenium. However, more data will be needed before impacts due to sediment can be determined.

2.4.3. Invertebrate Tissue Concentrations

The State Mussel Watch Program produces annual reports of concentrations of various pollutants in mussel tissues as an indication of contamination in the State's water bodies. Figure 2.2 shows Se concentrations in transplanted California mussels at various locations in Newport Bay, with the bold lines indicating range of concern levels. Selenium is found at a fairly constant level from 1993 to 1998. However, noticeable increases are observed in years 1999 and 2000. Compared with the food chain values in Table 2.3, the data for the last two years fall in the range of levels of concern. This warrants closer monitoring of bioaccumulation in the invertebrates in the future.

2.4.4. Fish Tissue Concentrations

Figure 2.3 shows selenium concentrations in fish tissues collected from San Diego Creek. Fish tissue analysis showed that water contents in fish were found to range from 73% to 79%. The data shown were calculated from wet weight concentrations using 75% for water content. Comparing with the values in Table 2.3, these concentrations fall in the range of levels of concern for fish.

In Newport Bay, fish tissue concentrations are generally lower than those found in the Creek (see Figure 2.4) and they are lower than the level of concern for fish in Table 2.3. An observation of the data is that fish tissue concentrations are generally lower than concentrations in mussel tissues from the Bay. The fish tissue concentrations both in the Creek and the Bay are well below a screening value of 20 mg/kg (dry weight) for fish tissue contamination established by Office of Environmental Health Hazard Assessment (OEHHA) for protection of human consumption (OEHHA, 1999).

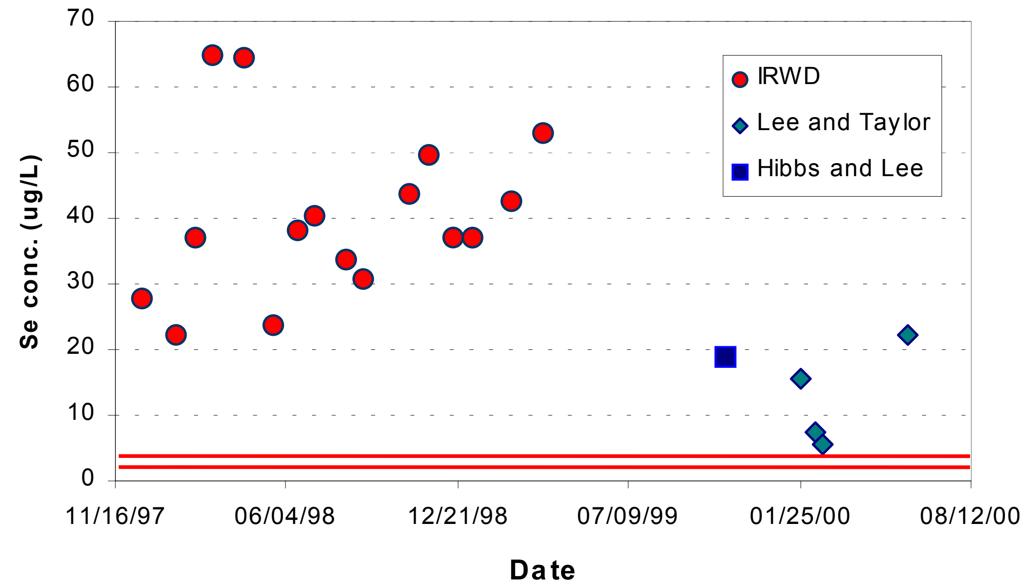


Figure 2.1 Water column concentrations at Campus Drive in San Diego Creek. Bold lines indicate the range of concern level (see Table 2.3).

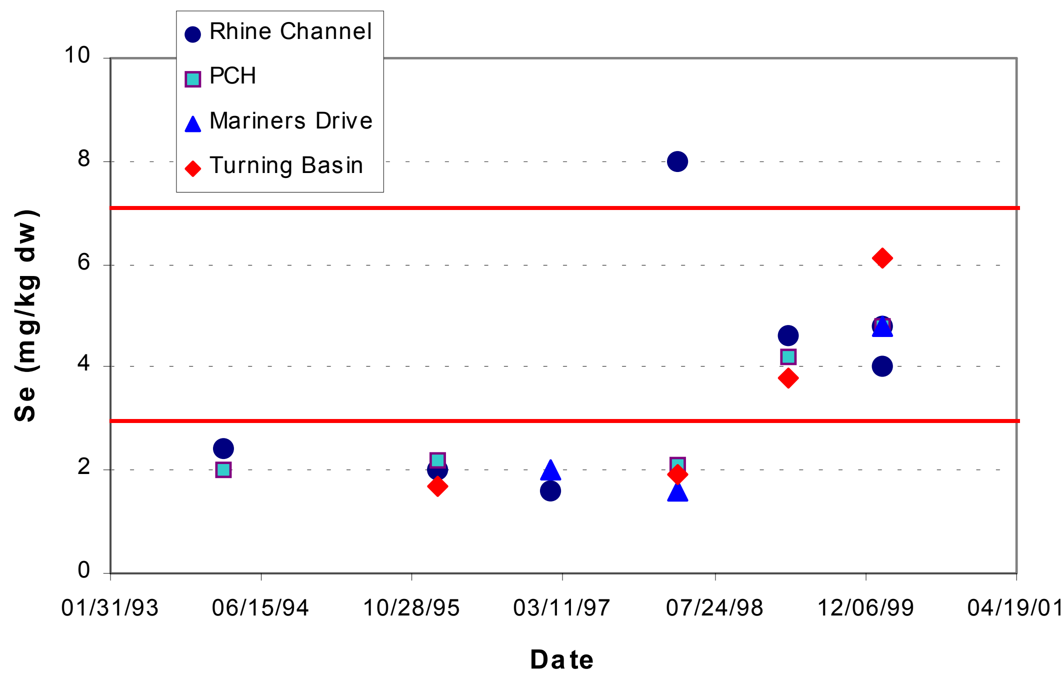


Figure 2.2 Selenium concentrations in transplanted California mussel tissues collected from Newport Bay (data source: SMWP). Bold lines indicate the range of concern level (see Table 2.3).

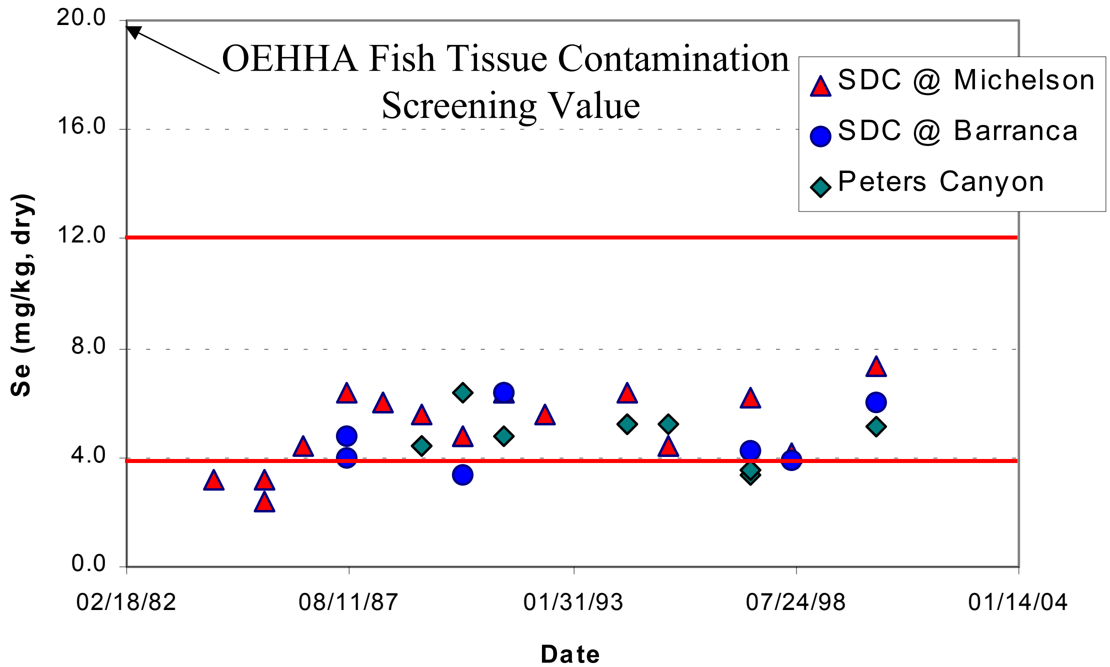


Figure 2.3. Whole body fish tissue concentrations of selenium in Red Shiners collected from San Diego Creek (data source: TSMP). Bold lines indicate the range of concern level (see Table 2.3).

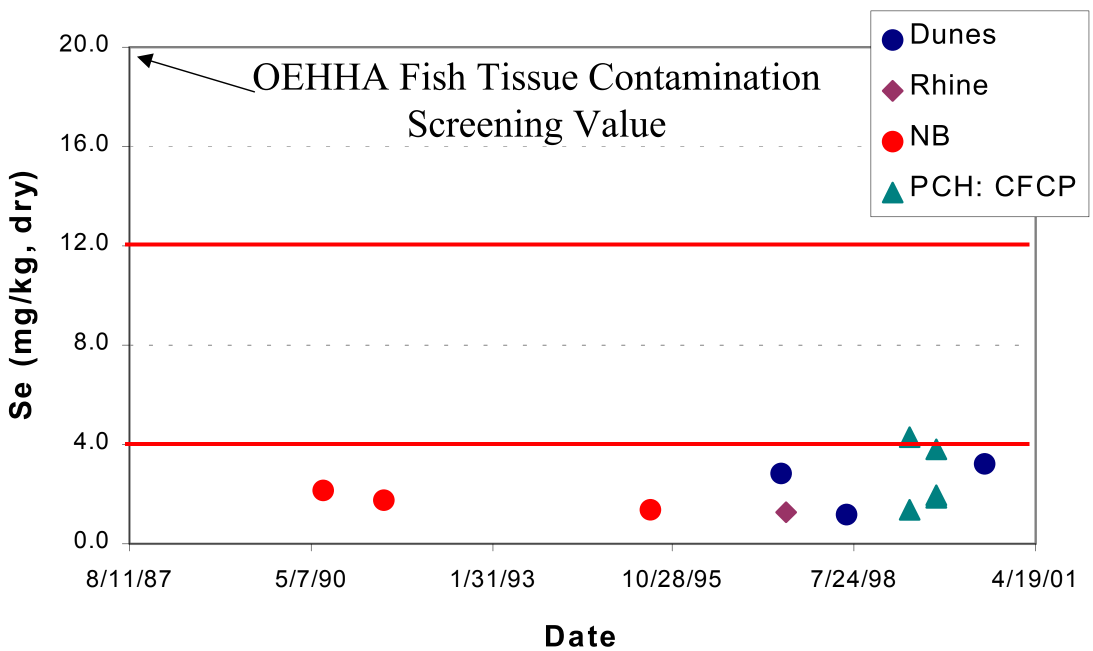


Figure 2.4. Fish filet tissue concentrations of selenium collected from Newport Bay (data source: TSMP). Bold lines indicate the range of concern level (see Table 2.3).

3. NUMERIC TARGETS

3.1. BENEFICIAL USES

The Water Quality Control Plan for the Santa Ana Region (Basin Plan, 1995) designates the following beneficial uses for Newport Bay, San Diego Creek and its tributaries (Table 3.1)

Table 3.1. Designated beneficial uses for Newport Bay and San Diego Creek watershed.

Water Body	BENEFICIAL USE																			
	MUN	AGR	IND	PROC	GWR	NAV	POW	REC1	REC2	COMM	WARM	LWRM	COLD	BIOL	WILD	RARE	SPWN	MAR	SHEL	EST
Lower NB	+					x		x	x	x					x	x	x	X	x	
Upper NB	+							x	x	x				x	x	x	x	X	x	x
San Diego Creek Reach 1	+							x	x		x				x					
San Diego Creek Reach 2	+							I	I		I				I					
Tributaries of San Diego Creek	+							I	I		I				I					

x present or potential beneficial use
I intermittent beneficial use
\+ excepted from MUN

3.2. NARRATIVE OBJECTIVES

To protect the designated beneficial uses, the Basin Plan includes the following narrative objectives for toxic substances:

Enclosed Bays and Estuaries

Toxic substances shall not be discharged at levels that will bioaccumulate in aquatic resources to levels which are harmful to human health.

The concentrations of toxic substances in the water column, sediments or biota shall not adversely affect beneficial uses.

Inland Surface Waters

Toxic substances shall not be discharged at levels that will bioaccumulate in aquatic resources to levels which are harmful to human health.

Toxic concentrations of contaminants in waters which are existing or potential sources of drinking water shall not occur at levels which are harmful to human health.

The concentrations of toxic pollutants in the water column, sediment or biota shall not adversely affect beneficial uses.

Groundwater

All waters of the region shall be maintained free of substances in concentrations which are toxic, or that produce detrimental physiological responses in human, plant, animal or aquatic life.

3.3 NUMERIC OBJECTIVES

As stated in the Problem Statement section of this report, USEPA promulgated CTR numeric standards for toxic substances to protect beneficial uses of water bodies in California (see Table 2.2). However, the chronic criterion for fresh waters (*i.e.*, 5 μg/L) is not considered to be fully protective of fish and wildlife resources by the US Fish and Wildlife Service (USFWS). In response to EPA's request for a formal consultation on the California Toxics Rule, USFWS prepared a biological opinion document on the effects of the promulgation of the CTR on the listed species and critical habitats in California (USFWS, 2000). USFWS found that the CCC for fresh waters did not protect listed fish and wildlife dependent on the aquatic ecosystem for development and/or foraging. The opinion was formed based on extensive review of experimental and field data conducted over the past decade. The USFWS believes that the weight of scientific evidence supporting a chronic criterion for selenium of ≤ 2 μg/L is now overwhelming. Therefore, USFWS recommended that a chronic criterion of 2 μg/L should be established. USEPA and USFWS have agreed on the following terms and conditions ("Services" refers to Fish and Wildlife Service and National Marine Fisheries Service)

> *EPA has agreed to revise its recommended 304 (a) acute and chronic aquatic life criteria for selenium by January 2002. EPA will propose revised acute and chronic aquatic life criteria for selenium in California by January of 2003. EPA will work in close cooperation with the Services to evaluate the degree of protection afforded to listed species by the revisions to these criteria. EPA will solicit public comment on the proposed criteria as part of its rulemaking processes, and will take into*

account all available information, including the information contained in the Services' opinion, to ensure that the revised criteria will adequately protect federally listed species. If the revised criteria are less stringent than those proposed by the Services in the opinion (i.e., 2 μg/L), EPA will provide the Services with a biological evaluation/assessment on the revised criteria by the time of the proposal to allow the Services to complete a biological opinion on the proposed selenium criteria before promulgating final criteria. EPA will provide the Services with updates regarding the status of EPA's revision of the criterion and any draft biological evaluation/assessment associated with the revision. EPA will promulgate final criteria as soon as possible, but no later than 18 months, after proposal... (USFWS, 2000)

3.4 SELECTED TARGET AND CURRENT CONDITION

For the purposes of the TMDL, the USFWS recommended criterion 2 μg/L is used in this report as the numeric target to ensure protection of aquatic species and wildlife in the San Diego Creek watershed. Attainment of this criterion in San Diego Creek, Santa Ana-Delhi Channel, and other Newport Bay tributaries will result in attainment of the saltwater standards in the Newport Bay (see Table 2.2). Recent measurements of selenium at Campus Drive in San Diego Creek and Irvine Avenue in Santa Ana-Delhi Channel show violation of the chosen numeric target (Table 3.2).

Table 3.2 Recent measurements of selenium in San Diego Creek and Santa Ana-Delhi Channel. Unit: μg/L

Location	Lee *et al.* 5/31/00	Hibbs 10/31/99	IRWD 12/97–3/99[a]
SDC, Campus Dr.	22.1	19	42.5
SA-Delhi, Irvine Ave.	11.9	---	---

[a]arithmetic average of the period indicated

4. SOURCE ANALYSIS

In southern California, a Mediterranean climate prevails, with dry summer and wet winter seasons. As a result, water bodies typically experience distinctly different seasonal flows and pollutant loads. However, regular monitoring data for selenium in Newport Bay and its watershed are not available. In stead, a few intense studies during short periods provide most of our current understanding of the selenium loading in this watershed. Reasonable estimation of annual and seasonal loads is not always feasible for each data set. Therefore, daily loads are also used for evaluating the significance of each different source (*e.g.*, groundwater vs. surface water) and comparing data among different data sets.

4.1. SURFACE WATERS AND GROUNDWATER

IRWD's monthly monitoring data from 12/1997 to 3/1999 (Figure 2.1) indicate consistent violation of the numeric target (2 μg/L) in San Diego Creek at Campus Drive. Figure 4.1 shows selenium concentrations in relation to flow rate. No strong correlation is found. However, daily loads estimated from concentrations and flow data seem to exhibit a pattern when plotted as a function of flow rate (Figure 4.2). In general, the estimated daily load shows an increasing trend with flow rate at the low end of the flow spectrum. There are too few data to determine the load pattern at high flow rates.

The monitoring data at Campus Drive allow an estimation of loading to Newport Bay. A statistical method is used to calculate seasonal and annual loads. The calculation methodology is summarized in Appendix A. The annual load of selenium is estimated to be 3248 lbs/year (4/1/98 - 3/31/99) with dry season load of 1227.4 lbs (4/1/98 - 9/30/98) and wet season load of 2020.6 lbs (10/1/98 – 3/31/99). Detailed calculations and data used are listed in Table A2 (Appendix A).

4.2. SELENIUM SOURCE IDENTIFICATION STUDY

Hibb and Lee (2000) investigated sources of selenium in the NB/SDC watershed. The study area is shown in Figure 4.3. The study presents convincing evidence that groundwater is a significant source of selenium to San Diego Creek and Newport Bay. At the watershed scale, the study results show that selenium concentrations exceed the numeric target in most of the surface and groundwater samples collected, and that they exhibit spatial heterogeneity (Figure 4.4). Concentrations in groundwater range from below 4 ppb (detection limit of the analytical method employed) to 478 ppb. A statistical analysis shows that selenium concentrations in groundwater samples were generally found to be higher within the boundaries of an historical marsh than in other areas. Radioisotope analysis on the water samples suggested that high selenium suggested that high selenium concentrations in groundwater result from underground soils in the saturated zone.

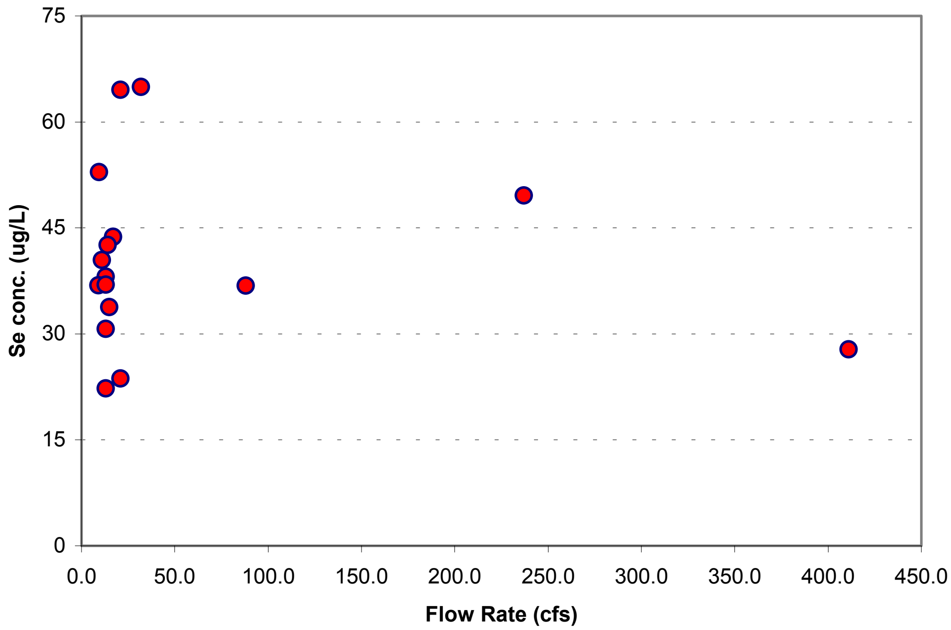


Figure 4.1 Relationships between dissolved selenium concentration and flow rate at Campus Drive in San Diego Creek (Se data: IRWD, flow data: OCPFRD).

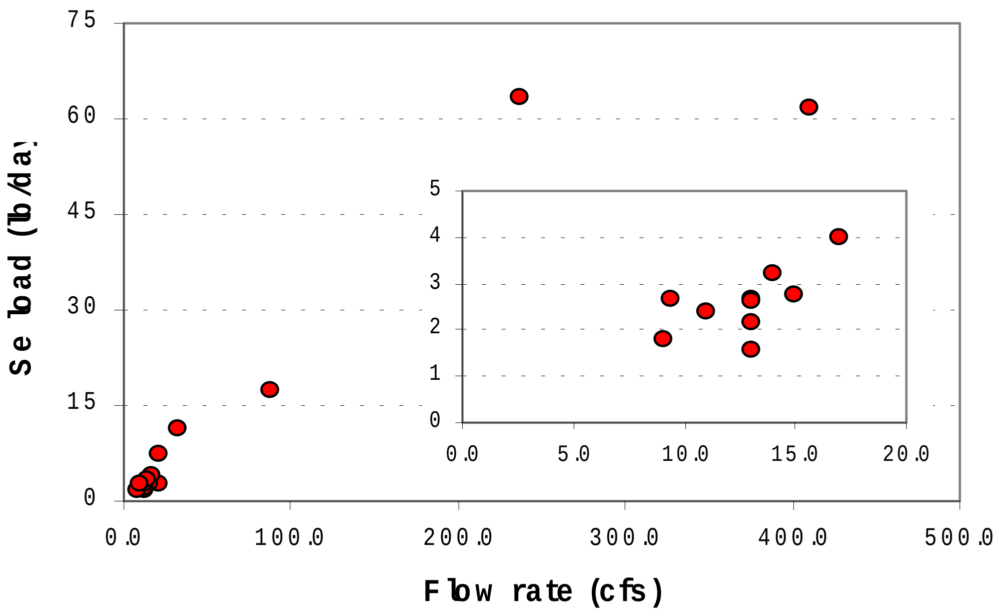


Figure 4.2 Estimated selenium daily load as a function of flow rate at Campus Drive in San Diego Creek (Se data: IRWD, flow data: OCPFRD).

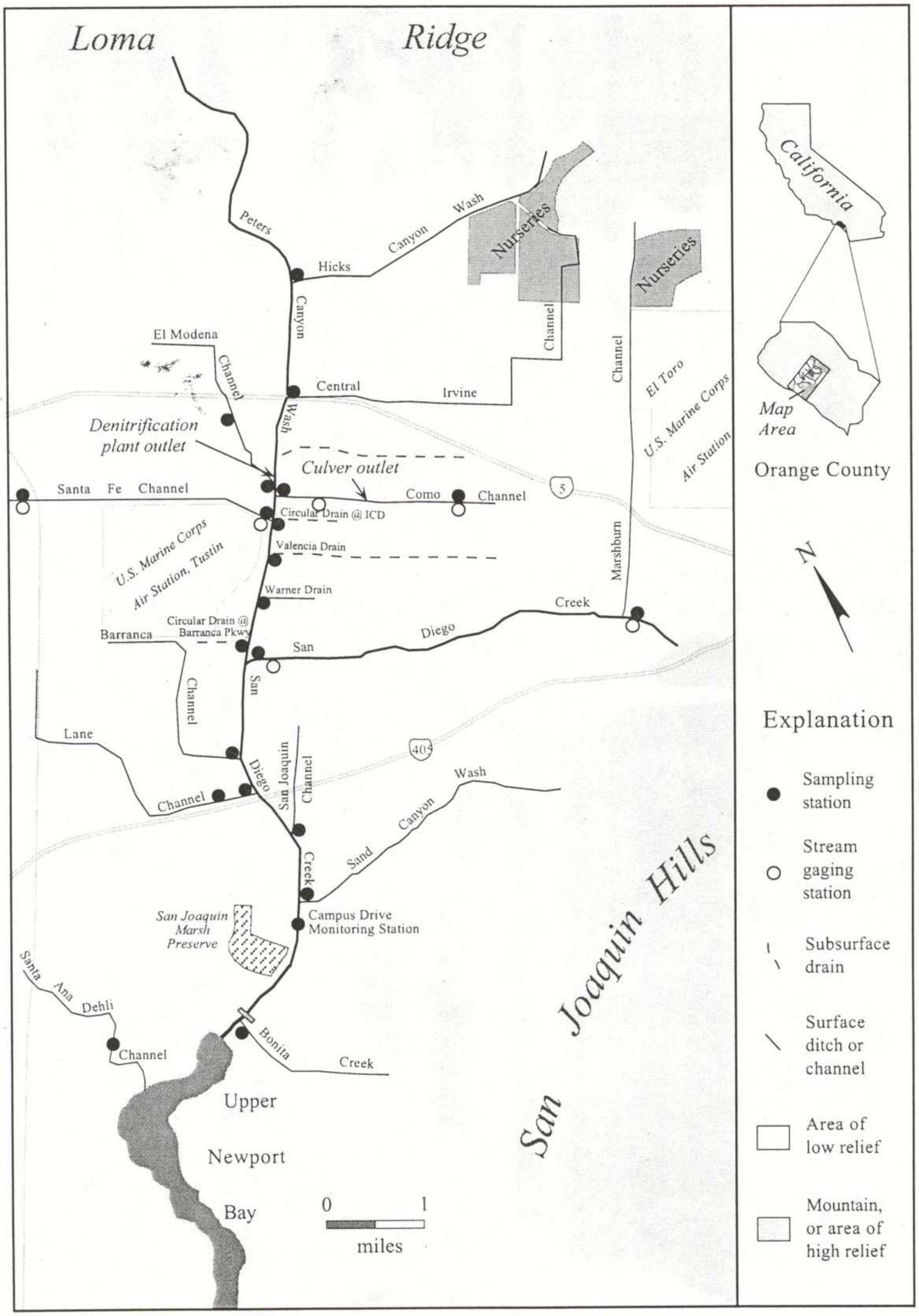


Figure 4.3. Map of study area, showing the locations of water sampling stations and stream gage stations on important channels and creeks (source: Hibbs and Lee, 2000).

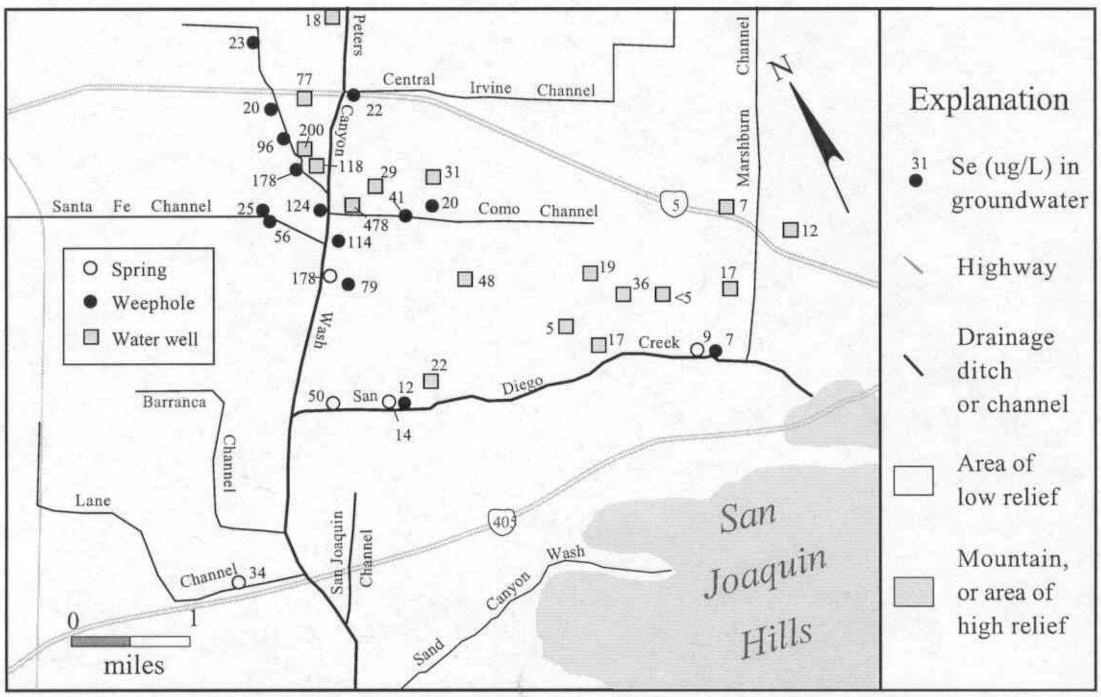


Figure 4.4. Selenium concentrations in groundwater (μg/L). Sample points include water wells, weepholes, and springs (data source: Hibbs and Lee, 2000).

Monitoring of nursery discharge shows selenium concentrations in most of runoff samples (6 out of 7) were below detection limits (*i.e.*, < 4 μg/L). One sample was detected at 7 μg/L from Bordiers Nursery. Surface water monitoring shows that discharges containing less than 10 μg/L selenium were mostly urban and agricultural runoff. Surface channels and drains with particularly high concentrations coincide with areas where high selenium groundwater samples are found. Those channels include Como Channel (38 to 42 μg/L), Valencia Drain at Moffett Drive (25 to 40 μg/L), Warner Drain (24 to 33 μg/L), and the circular drains at Irvine Center Drive (141 to 162 μg/L) and at Barranca Parkway (107 μg/L). Channel inspection and chemical composition analysis indicate that those drainage channels collect considerable amounts of groundwater.

Three drainage channels (San Diego Creek above the confluence with Peters Canyon Channel, Como Channel, and Santa Fe Channel) were selected for detailed flow and chemical investigation. In these three channels, stream flows were measured at upstream and downstream gage stations. Results indicated that these channels are gaining streams in the reaches studied. Namely, the increases in flow rates result from seepage of groundwater into the surface channels.

An analysis of the flow and concentration data indicates the significance of groundwater as a selenium source. Total selenium load from groundwater in these three reaches is approximately 0.36 lbs/day. The surface water loading of

Se at Campus Drive falls in a range from 1.6 to 4 lbs/day at low flow conditions (see Figure 4.1). The comparison shows that groundwater inputs to the three reaches alone represent a significant portion (9 to 22%) of the total Se load to Newport Bay, indicating the significance of groundwater input of Se to surface water. Detailed calculations are summarized in Table B2 (Appendix B).

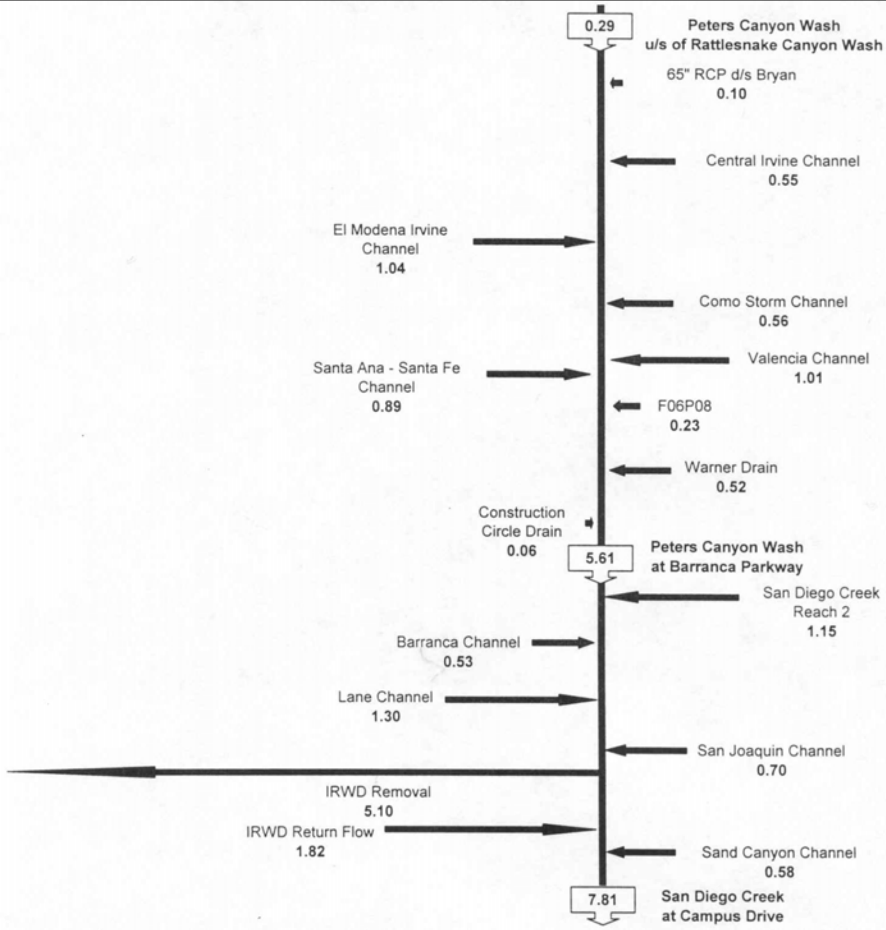
Results of the study suggest that discharges from groundwater cleanup projects and shallow groundwater dewatering activities are potential sources of selenium and could be significant depending on the locations of these activities. However, selenium information is not available for these discharges.

4.3. OCPFRD SEPTEMBER 1999 PETERS CANYON WASH/SAN DIEGO CREEK NUTRIENT STUDY (OCPFRD, 2000)

As part of the investigation of nutrient sources in the San Diego Creek watershed, OCPFRD conducted an one-week program of measurements of flow rate in tributaries of Peters Canyon Channel and reaches 1 and 2 of San Diego Creek in September 1999. The flow information allows estimation of groundwater flow inputs to surface channels at the watershed scale. Results show that the net increase in flow at Barranca Parkway in Peters Canyon Channel was approximately 0.36 cfs in the reach studied. Increases in San Diego Creek were 1.32 and 0.79 cfs for reach 1 and reach 2, respectively. These net flow increases, calculated by subtracting measured creek flow from its tributary flows, are believed to be contributions from groundwater via seepage and weep holes. The net flow increases total 2.47 cfs, which represents a significant portion of the Creek at Campus Drive. It should be noted that the overall contribution of groundwater to surface flow is expected to be larger since inputs of groundwater to the tributaries (*e.g.*, Como and Santa Fe Channels, Table B2 in Appendix B) are not accounted in the calculation.

4.4. CWA SECTION 319H STUDY MONITORING DATA

A more recent study (Lee and Taylor, 2001) was conducted by Dr. Fred Lee and Scott Taylor, RBF, to investigate sources of acute toxicity in the San Diego Creek watershed. Samples were collected on four days in 2000 – 01/25, 02/12, 02/21, and 05/31. The sampling in January and February occurred during storm events and the January sampling represents a “first-flush” event, according to flow records. The May sampling provides information under dry weather conditions. Chemical analysis allows differentiation of dissolved and particulate selenium. Sampling stations and selenium concentrations are summarized in Appendix C. Generally speaking, the results suggest that water-borne selenium mostly existed



Q increase
(cfs)

0.36 (PCW)

0.79 (SDC R2)

1.32 (SDC R1)

Figure 4.5 Average daily flow rates (cfs) in tributaries to Peters Canyon Channel and reaches 1 and 2 of San Diego Creek, September 12-20, 1999 (data: OCPFRD, 2000).

in dissolved forms under low flow conditions. Particulate fractions (*i.e.*, total minus dissolved) of selenium during rain events fall in a wider range than those found in dry weather (5/31/00 samples). Consistent with other monitoring data, the measured concentrations exceed the numeric target at most of the locations.

There was only one sample collected on January 25, 2000 and the total selenium concentration was 15.6 μg/L at Campus Drive. Total selenium concentrations for the rest of the sampling days are shown in Figures 4.6 – 4.8. These figures show spatial distributions of selenium concentrations in the watershed and allow comparisons of loading from different tributaries. Table 4.1 lists estimated loads at four locations in the watershed. Several observations concerning Se sources are summarized as below:

1. During rain events, high concentrations were found at Hines Channel and Sand Canyon Channel during storms (Figures 4.6 and 4.7), suggesting that Se sources exist upstream of the sampling locations when rain events occur.

These sources may include runoff from hillside, open fields, agricultural lands, and nurseries. The high concentrations were diluted downstream as flows increased.

2. The dry weather sample collected in May (Figure 4.8) from Hines Channel shows a low concentration, which is consistent with the findings in Hibbs' study. This suggests that contributions from nursery channels to the watershed are small in dry weather.

3. The estimated loads indicate that San Diego Creek contributes a substantially higher Se load to the Bay than Santa Ana-Delhi channel. Of the load at Campus Drive, Peters Canyon Channel is the biggest contributor of selenium in the San Diego Creek watershed in dry weather. As noted in sections 4.2 and 4.3, the contribution is attributable to inputs of groundwater to PCC.

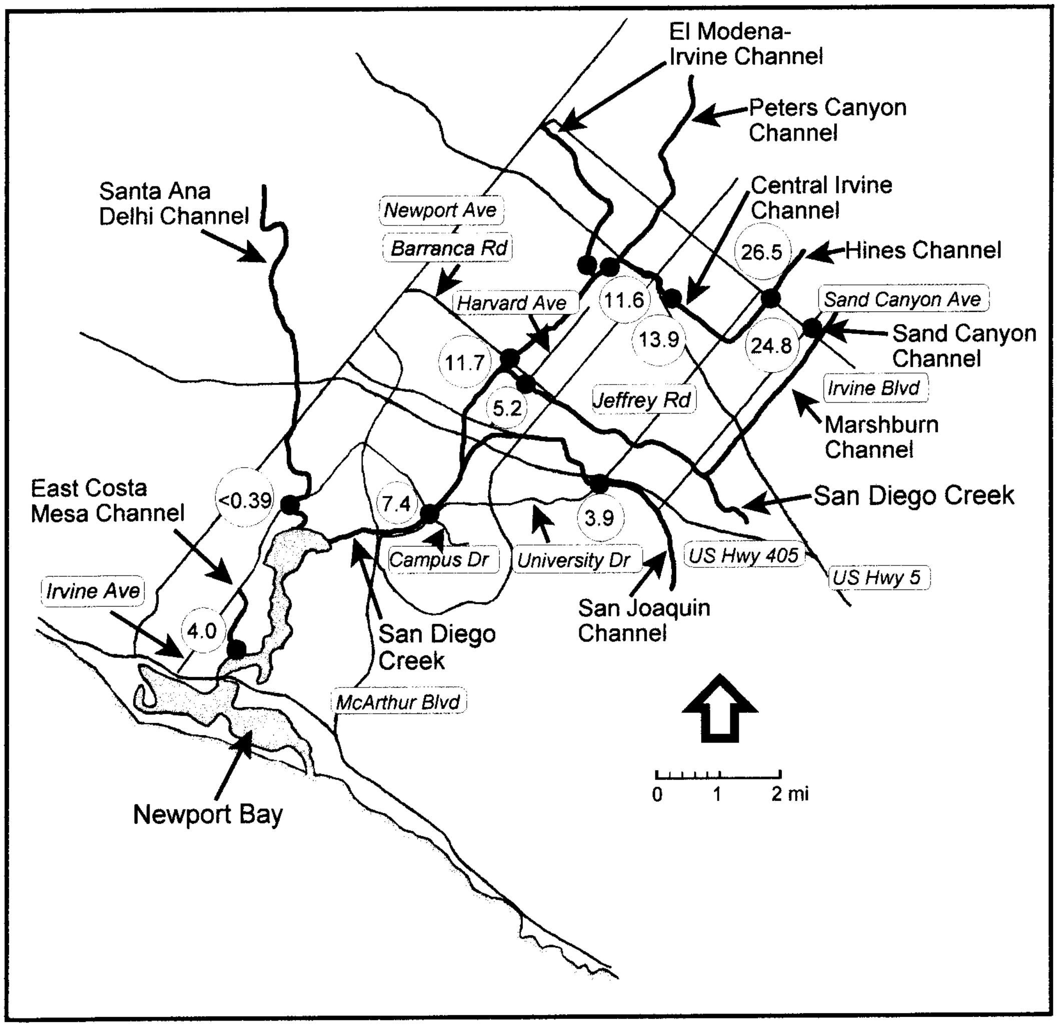
4. Se loads at Barranca Parkway in PCC did not change considerably between dry weather and rain events. The drainage area cover mostly urban land uses, suggesting that urban Se load is not significant.

5. Loading at Harvard Avenue in San Diego Creek increases substantially during rain events compared to that in dry weather condition. Estimated loads (Table 4.3) are comparable to those from PCC. The drainage area for Harvard Avenue in SDC covers more open space than that in PCC drainage area (see Appendix C for land uses). The seasonal variation in loading suggests that open space runoff is a potential source of Se during rain events.

Table 4.1 Calculated loads of selenium from major tributaries in Newport Bay/San Diego Creek watershed

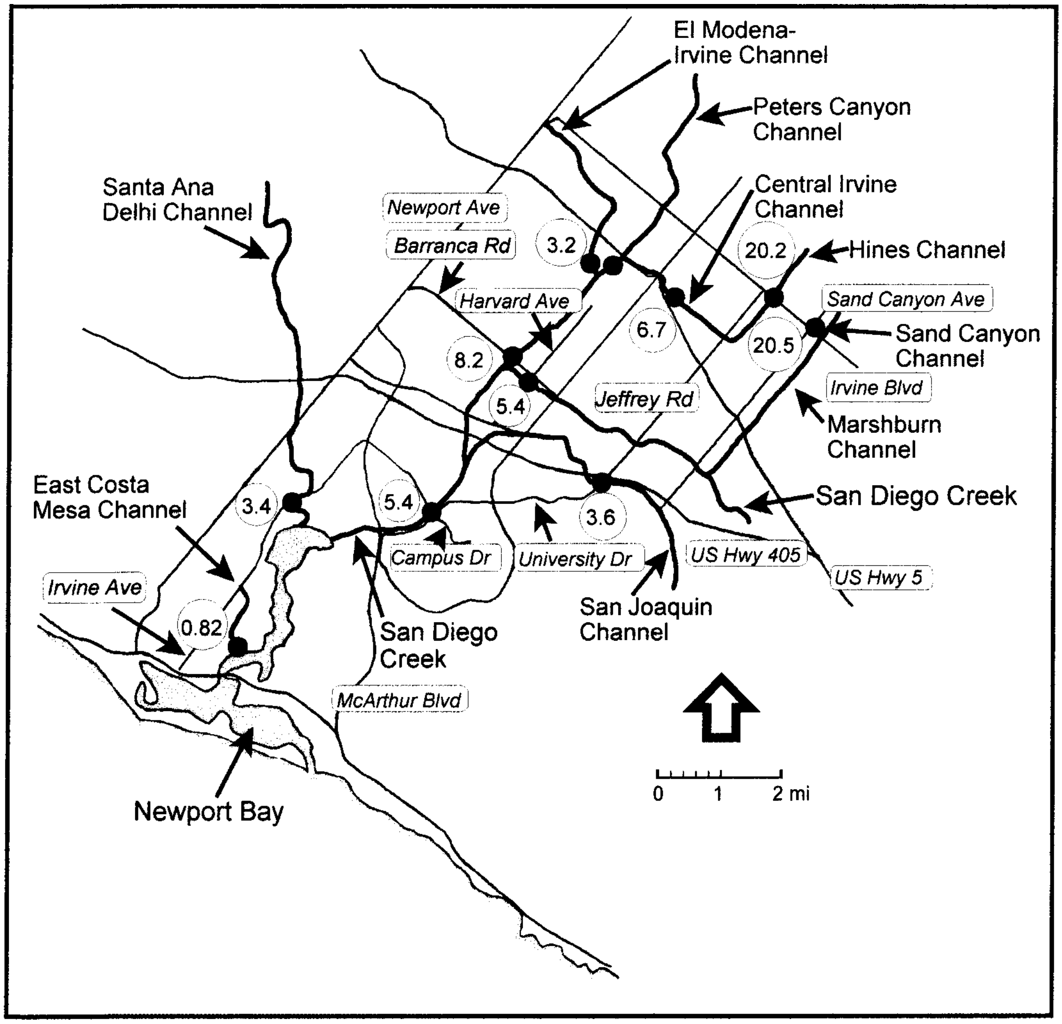
	SDC[a] @ Campus	SDC @ Harvard	PCC[b] @ Barranca	Santa Ana-Delhi
2/12/00				
Conc. (μg/L)	7.4	5.2	11.7	<0.39
Flow[c] (cfs)	96.5	49.9	30.8	23.7
Load (lbs/day)	**3.86**	**1.40**	**1.95**	**<0.05**
2/21/00				
Conc. (μg/L)	5.4	5.4	8.2	3.4
Flow[c] (cfs)	96.5	49.9	30.8	23.7
Load (lbs/day)	**2.81**	**1.45**	**1.36**	**0.44**
5/31/00				
Conc. (μg/L)	22.1	10.1	31	11.9
Flow[c] (cfs)	14.6	3.62	8.21	3.29
Load (lbs/day)	**1.74**	**0.20**	**1.37**	**0.21**

[a]San Diego Creek, [b]Peters Canyon Channel, [c]Monthly average flow rate



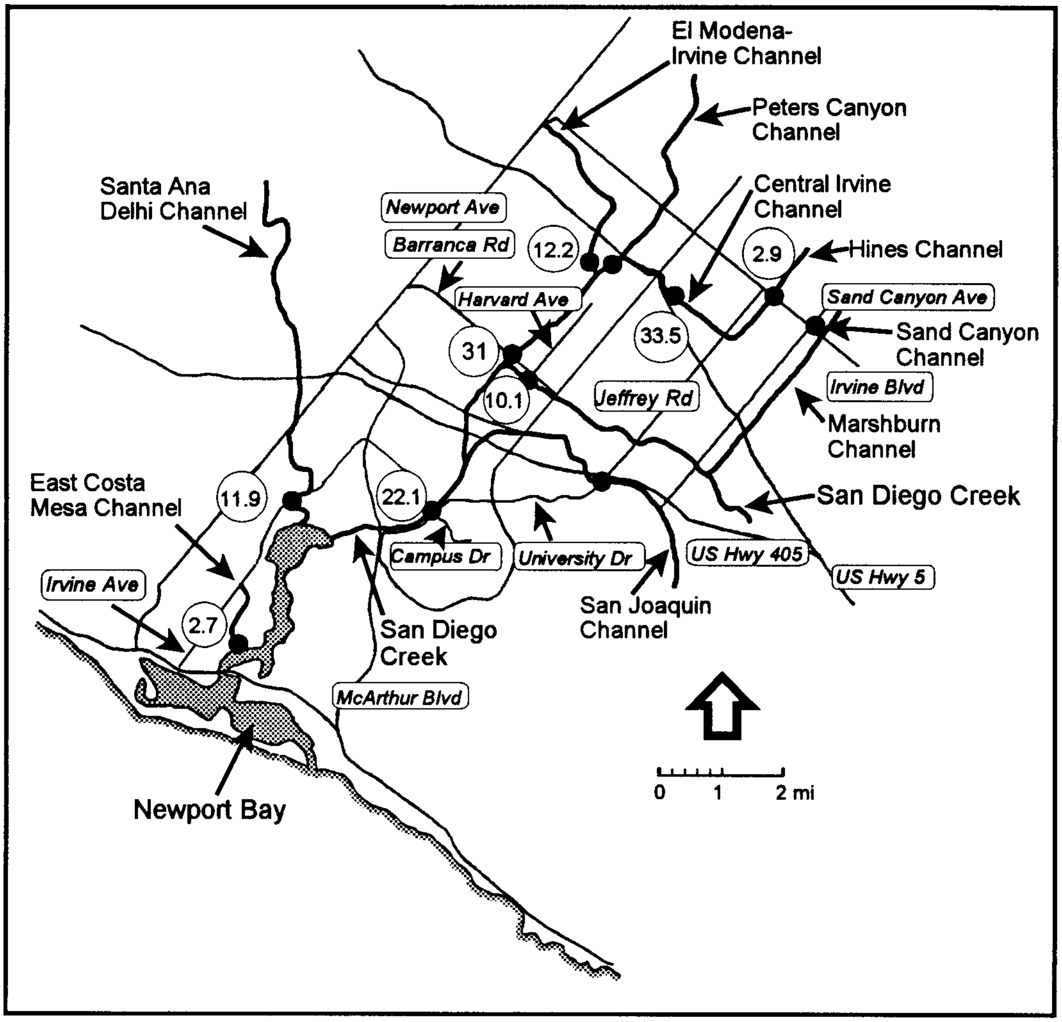
Total Selenium Concentrations (µg/L)
February 12, 2000
(Wet Weather Sampling)

Figure 4.6. Spatial distribution of total selenium concentrations during a storm on February 12, 2000 (data source: Lee and Taylor, 2001).



Total Selenium Concentrations (μg/L)
February 21, 2000
(Wet Weather Sampling)

Figure 4.7. Spatial distribution of total selenium concentrations during a storm on February 21, 2000 (data source: Lee and Taylor, 2001).



Total Selenium Concentrations (μg/L)
May 31, 2000
(Dry Weather Sampling)

Figure 4.8. Spatial distribution of total selenium concentrations on May 31, 2000 (data source: Lee and Taylor, 2001)

4.5. RESIDENTIAL RUNOFF REDUCTION (R3) STUDY

The R3 study was initiated in 2000 by a multi-agency workgroup to reduce the impact of urban residential runoff and conserve domestic and reclaimed water resources. The workgroup includes the Southern California Coastal Water Research Project (SCCWRP), the Municipal Water District of Orange County (MWDOC), National Water Research Institute (NWRI), Department of Pesticide Regulations (DPR), the Irvine Ranch Water District (IRWD), and Santa Ana Regional Water Quality Control Board (SARWQCB). The study identified five isolated residential communities to allow investigation of pollutant loading strictly from residential areas. As a part of the baseline monitoring, selenium concentrations in the runoff samples collected (11/28/00 to 7/3/01) were measured. Results show that all samples were below detection limits of the analytical methods used (1.5 μg/L and 5 μg/L). This suggests that urban runoff is not a significant source for selenium.

4.6. SOURCE FROM THE BAY

No data is available for determining if there exist sources of selenium in the Bay.

4.7. ATMOSPHERIC DEPOSITION

Deposition of selenium from the atmosphere is a part of the global cycling of selenium and it represents a source to the watershed. The physical constituents of atmospheric selenium are the particle phases, predominantly less than 1 μm in diameter (Duce *et al.*, 1976), and gaseous forms (Mosher and Duce, 1983). Gaseous atmospheric Se can bond to particulate material for long-range transport. Deposition of Se from the atmosphere to the global surface occurs in both wet and dry forms. Dry deposition accounts for the exchange of particulate and gaseous material between the atmosphere and the global surface. It is usually insignificant compared to wet deposition. Wet deposition refers to rainout and washout of all forms of atmospheric Se. It is the most important removal mechanism for selenium from the atmosphere to the earth surface. Reported rain concentrations in urban areas are in the range of 0.1 to 0.4 μg/L (Mosher and Duce, 1989). Selenium load due to rainfall is then estimated to be 1.43 lbs/year to the Bay (1363.6 acres, open water area) assuming rainfall concentration of 0.4 μg/L and annual rainfall of 11.6 in (historical average at Newport Beach Harbor Master station, OCPFRD). Therefore, atmospheric deposition is insignificant compared to the load at Campus Drive in San Diego Creek.

4.8. OCEANIC SOURCE

No data is available for selenium concentrations in Southern California ocean water. On the global scale, average dissolved selenium concentrations are 0.03 μg/L and 0.095 μg/L in the surface mixed layer of oceans and in deep oceans, respectively (Nriagu, 1989). In Northern California, dissolved selenium was reported to be 0.1 µg/L at Golden Gate in San Francisco Bay (San Francisco Estuary Institute, 1997). These reported levels of selenium fall below the concern level for water in Table 2.3 and CTR criteria for marine waters in Table 2.2. Therefore, selenium input from seawater is not expected to be significant.

4.9. ANALYSIS SUMMARY

In summary, existing data are limited for thorough study and investigation of the sources and impacts of selenium to Newport Bay/San Diego Creek watershed. The data available allow preliminary assessment of the problem. Conclusions of the analysis in this report are summarized as follows:

1. IRWD's monitoring data allow analysis of relationship among concentration, load, and flow rates. The monthly monitoring data at Campus Drive shows no apparent trend between concentration and flow rate. Daily load increases with flow rate and seems to reach a plateau at high flow rates during large storms. However, there were only two data points greater than 100 cfs and they are not sufficient to determine a trend at the high end of the flow spectrum. Statistical analysis of the data estimates that annual load was 3248 lbs from 4/1/98 to 3/31/99 with dry load 1227.4 lbs (4/1/98 – 9/30/98) and wet load 2020.6 lbs (10/1/98 – 3/31/99).

2. Dr. Barry Hibbs' study provides convincing evidence that shallow groundwater is a significant source of selenium to surface waters in the San Diego Creek watershed. Flow increases in three drainage channels selected were attributable to contributions from groundwater. Measurements of selenium concentrations were found to be substantially higher downstream in these channels than upstream as a result of groundwater inputs. Load calculation indicates that the significance of the loading from the groundwater inputs at these three channels to the total loading at Campus Drive. Surface channels associated with high Se concentrations coincide with areas where high groundwater water concentrations of Se were found, namely, the general area of Peters Canyon Channel and its tributaries. This also suggests that groundwater cleanup and dewatering operations could be significant sources of selenium to the watershed.

3. OCPFRD's investigation of nutrient sources reveals the magnitude of groundwater flow input to surface water. Three major reaches (Peters Canyon Channel, both reaches of San Diego Creek) all contain significant amounts of groundwater in the channel flows.

4. The 319h study for identifying toxicity source in San Diego Creek watershed by Dr. Fred Lee *et al.* provides spatial distributions of selenium concentrations in the watershed. San Diego Creek contributes the largest load of selenium to Newport Bay. Of the load from San Diego Creek, Peters Canyon Channel

which collects selenium from selenium-laden shallow groundwater, represents the major source. Nursery channels showed low concentrations in dry weather. However, high concentrations were found in the channels during rain events, suggesting sources existing upstream of the channels. These sources may include runoff from hillsides, open spaces, agricultural lands, and commercial nursery sites. Further studies are needed to identify the sources. During rain events, the Se load from SDC reach 2 was comparable to that from Peters Canyon Channel, suggesting runoff from open space /or agricultural lands is a potential source in wet weather.

5. Atmospheric deposition of selenium is not significant compared to loading from San Diego Creek and other tributaries. Selenium concentration in seawater is unlikely to cause ecological impacts.

5. LINKAGE ANALYSIS

5.1. INTRODUCTION

The linkage analysis describes the relationship between the numeric targets and the total assimilative capacity (or loading capacity) of the waterbody. The loading capacity of the watershed is the maximum amount of a pollutant allowed to be discharged into the watershed while the numeric target(s) can still be achieved. In this section, loading capacities are calculated and related to the numeric target for selenium.

5.2. METHODOLOGY

As stated in Source Analysis, waterbodies in Southern California are subjected to distinctly different seasonal flows and pollutant loads. For the purpose of characterizing pollutant loads, the temporal variations are portrayed as dry and wet seasons, which cover periods of 4/1-9/30 and 10/1-3/31, respectively. Average flows for dry and wet seasons are calculated using five year flow records (94-95, and from 96-97 to 99-00; 95-96 flow data are not available). An implicit assumption is that, statistically, flow patterns in terms of magnitudes and frequencies will repeat in the future. Consistent with the Nutrient TMDL adopted by Regional Board (Resolution No. 98-9, as amended by Resolution No. 98-100), high flows (50 cfs or more as measured at SDC @ Campus Drive, and 5 cfs or more in SA-Delhi @ Irvine Ave.) during storms are excluded from the calculation of loading capacities since Se is thought to be flow out of the ocean without substantial mixing. The cutoff flow of 50 cfs established for SDC (Campus Drive) exceeds ~97% of the flows in dry season and ~84% of the flows in wet season based on the five-year flow records used. Similarly, the 5 cfs for Santa Ana-Delhi covers 94% of flows in dry season and 77% in wet season.

Loading capacities are calculated such that USFWS's criterion (*i.e.*, 2 μg/L dissolved) is to be attained. The calculated loading capacities are listed in Table 5.1 along with average flow information.

Table 5.1 Average flows and loading capacities for dry and wet seasons for San Diego Creek (Campus Drive) and Santa Ana-Delhi Channel (Irvine Ave.)

	Dry Season (4/1-9/30)	Wet Season (10/1-3/31)	Annual
San Diego Creek			
Average flow[a] (cfs)	15.2	15.4	
Loading capacity[a] (lbs)	29.1	25.4	54.5
Santa Ana-Delhi Channel			
Average flow[b] (cfs)	2.18	2.21	
Loading capacity[b] (lbs)	4.03	3.35	7.38
Total loading capacity (lbs)	33.13	28.75	61.88

[a]Only apply to flows below 50 cfs and flows above 50 cfs, but not as a result of precipitation
[b]Only apply to flows below 5 cfs and flows above 5 cfs, but not as a result of precipitation

6. ALLOCATIONS

6.1 INTRODUCTION

An EPA document "Guidance for Developing TMDLs in California" (EPA Region 9, 2000) specifies that TMDL documents must identify the following components: appropriate wasteload allocations for point sources and load allocations for nonpoint sources and natural background. The guidance document also specifies that the TMDL and associated wasteload and load allocations must be expressed in quantitative terms. In addition, an explicit and/or implicit margin of safety (MOS) must be specified to account for technical uncertainties in establishing the TMDL. In this section, allocations are calculated and assigned for point sources and nonpoint sources based on the following TMDL equation.

$$\text{TMDL} = \Sigma \text{ (Load Allocations)} + \Sigma \text{ (Wasteload Allocations)} + \text{MOS}$$

6.2 MARGIN OF SAFETY

Most of the uncertainty associated with calculation of the TMDL for selenium relates to flow rates. The average flow rates for dry and wet seasons were calculated using five years of flow data (94-95, and from 96-97 to 99-00; 95-96 flow data is not available). An implicit assumption of the calculation is that statistically, the flow pattern in the past five years will repeat in the future. The inherent variations of the flow pattern will propagate to the estimation of the TMDL. In addition, technical uncertainty such as that associated with flow rate measurements contributes to the uncertainty of estimating the TMDL.

In this report, an explicit margin of safety is used to account for these technical uncertainties. The margin of safety is set at 5% of the annual load (3.1 lbs/year). Conservative approaches for calculating the TMDL in this report include:

- USFWS's recommended criterion (2 μg/L, dissolved) is chosen over the CTR criterion (5 μg/L) for the numeric target and is used for the calculation of loading capacity (dry and wet seasonal loading).

- Attainment of 2 μg/L in San Diego Creek and other Newport Bay tributaries will clearly result in attainment of the much less stringent saltwater standards in Newport Bay (see Table 2.2), considering dilution of the creek flow in the Bay.

6.3 ALLOCATIONS

6.3.1 Load Allocations

EPA's regulation requires individual load allocations be assigned to specific nonpoint sources unless doing so would not be feasible (40 CFR, 130.32(b)). In cases where it was not feasible to assign individual load allocations, specific nonpoint sources can be grouped together into categories or subcategories. Each category or subcategory would then be given a load allocation.

6.3.2 Wasteload Allocations

An individual wasteload allocation is required to be assigned to each point source covered by the NPDES permit program (40 CFR 130.32(b)). Two exceptions are listed in the Federal Rule:

a) One waste load could be allocated to a category or subcategory of sources within a waterbody subject to a general permit under the NPDES program.
b) Pollutant loads from permitted facilities that did not need to be reduced in order to achieve water quality standards could be grouped into one category or subcategory, or considered as part of background loads.

Figure 6.1 shows sources of selenium in the watershed. The significance of these sources varies, in part depending on the location of discharges and the season of the year (see discussion in Source Analysis). In general, groundwater seepage/infiltration represents a significant and constant source. Runoff from open space, hillsides, and agricultural lands could be significant sources during rain events. Nursery runoff shows relatively low concentrations (< 7 μg/L) in dry weather and are potential sources during storms.

Discharges from groundwater cleanup and dewatering could be significant sources and loading from those operations depends on their location. However, the quantification of loading from individual discharges is not feasible for lack of information on selenium concentrations in effluents from those operations. In this report, allocations are assigned to groundwater cleanup and dewatering as groups pursuant to the Federal Regulations (40 CFR, 130.32(b)). Monitoring of flow and concentrations in discharges from cleanup and dewatering operations will be required as part of an implementation plan for this TMDL. The implementation will be developed following promulgation of the TMDL. Allocations for individual discharge will then be assigned based on the monitoring data.

Urban runoff is found to contain very low Se concentrations (< 1.5 μg/L). Contribution from atmospheric deposition is negligible compared with other sources. However, accurate quantification of loading from the sources is not feasible due to limited data available. In this report, wasteload and load allocations are assigned based on the following general guidelines:

- Allocations among source categories are assigned based on the data available, such as concentrations, flows, loading (see Source Analysis section), and/or acreage of land uses. In general, significant sources require larger reductions in loading than minor sources to attain the numeric target.

- Within the same source category, allocations for individual dischargers are prorated based on area (*e.g.*, nurseries).

- Allocations are season-dependent and are assigned based on the nature of each source. For example, runoff from hillside, open space, and agricultural lands is minimal in dry season but could be significant in terms of loading during rain events. Loading form shallow groundwater water is likely to change because creeks may change from gaining streams to losing streams as a result of high water level in the creeks during rain events.

- Atmospheric deposition and urban runoff are removed from the allocation scheme due to low loading from these two sources.

Table 6.1 shows wasteload and load allocations, and a compliance schedule. The schedule calls for evaluation of compliance with target loads specified for each source category once every five years. The estimated current load is considered as the current load of selenium at Campus Drive based on IRWD's monitoring data (4/98-3/99) based on IRWD's monitoring data (4/98-3/99). The 2007 and 2012 annual target loads are set to achieve 50% and 75% reduction of the 98-99 annual load. The numeric target is to be attained by 2017.

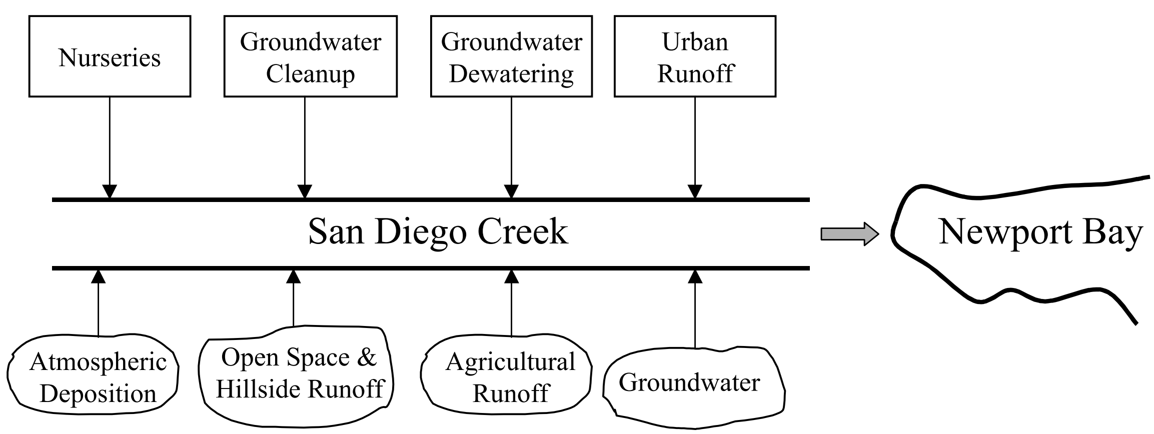


Figure 6.1 Sources of selenium in the Newport Bay/San Diego Creek watershed. Sources in boxes are point sources currently under regulatory permits, and others are non-point sources.

Table 6.1 Wasteload and load allocations of selenium for Newport Bay Watershed.

Source	4/98-3/99 Loading	2007 Dry Season	2007 Wet Season	2007 Annual Allocation	2012 Dry Season	2012 Wet Season	2012 Annual Allocation	2017 Dry Season	2017 Wet Season	2017 Annual Allocation
	lbs/year	lbs/season	lbs/season	lbs/year	lbs/season	lbs/season	lbs/year	lbs/season	lbs/season	lbs/year
Wasteload Allocations (WLA)										
Groundwater Dewatering		78.3	67.9	146.2	39.2	33.9	73.1	4.4	4.2	8.6
Groundwater Cleanup		87.0	75.4	162.4	43.5	37.7	81.2	4.8	4.7	9.5
Hines Nursery		12.9	16.7	29.6	6.4	8.4	14.8	2.1	2.8	4.9
Bordiers Nursery		6.4	8.3	14.7	3.2	4.2	7.4	1.1	1.4	2.5
El Modeno Gardens		2.7	3.5	6.2	1.3	1.8	3.1	0.4	0.6	1.0
Nakase Nursery		4.0	5.2	9.1	2.0	2.6	4.6	0.7	0.9	1.5
AKI		0.9	1.1	2.0	0.4	0.6	1.0	0.1	0.2	0.3
Unpermitted nurseries		8.0	10.4	18.4	4.0	5.2	9.2	1.3	1.7	3.1
Nursery Sub-total				80.0			40.0			13.3
WLA Sub-total				388.6			194.3			31.5
Load Allocations (LA)										
Agriculture Runoff		78.3	71.6	149.9	39.2	35.8	75.0	4.6	5.0	9.6
Undefined Sources (open space and hillside runoff, shallow groundwater, in-bay Se)		591.6	493.9	1085.5	295.8	246.9	542.7	11.9	5.8	17.7
LA Sub-total				1235.4			617.7			27.3
Total	**3248**	870	754	**1624**	435	377	**812**	31.5	27.3	**58.8**

1. Dry season applied to the time period from 4/1 to 9/30, and wet season applies to the time period from 10/1-3/31
2. The 2017 total load = 61.88 lbs/yr – 3.1 lbs/yr (MOS) = 58.78 lbs/yr.
3. One pound of Se is roughly equal to $6*10^7$ gallons of discharge with Se concentration of 2 μg/L.

REFERENCES

Camp Dresser & Mckee, Inc., (1985) *Shallow Groundwater Investigation West Central Part of the Irvine Subbasin*, a report submitted to The Irvine Company.

Duce, R. A. *et al*., (1976) *Geophys. Res. Lett.*, vol. 3, pp. 339.

Enberg, R. A. *et al.* (1998) Federal and State Perspectives on Regulation and Remediation of Irrigation-Induced Selenium Problems, in *Selenium in the Environment*, Ed. by W. T. Frankenberger Jr. and Sally Benson, Marcel Dekker, Inc. New York, pp. 1-25.

Fowler, S. W., and Benayoun, G., (1976) Influence of Environmental Factors on Selenium Flux in Two Marine Invertebrates, *Mar. Biol*., vol. 37, pp. 59.

Henderson, J. D. *et al*. (1995) Assessing Selenium Contamination in two San Joaquin Valley, CA, Sloughs, US Fish and Wildlife Service, Region 1, Division of Environmental Contaminants, Sacramento, CA.

Hibbs, B. J., and Lee, M. M. (2000) Sources of Selenium in the San Diego Creek Watershed.

Lee, F. G. and Taylor S. (2001) Results of Aquatic Toxicity Testing Conducted During 1999-2000 in the Upper Newport Bay Watershed.

Lemly, A. D. (1993) Guidelines for Evaluating Selenium Data from Aquatic Monitoring and Assessment Studies, *Environmental Monitoring and Assessment*, vol. 28, pp. 83-100.

Lemly, A. D. (1995) A Position Paper on Selenium in Ecotoxicology: A Procedure for Deriving Site-Specific Water Quality Criteria, *Ecotoxicology and Environmental Safety*, vol. 39, pp. 1-9.

Luoma, S. N. *et al*., (1992) Determination of Selenium Bioavailability to a Benthic Bivalve from Particulate and Solute Pathways, *Environ. Sci. Technol.*, vol. 26, pp. 485-491.

Luoma, S. N. and Presser, T. S. (2000) *Forecasting Selenium Discharges to the San Francisco Bay-Delta Estuary: Ecological Effects of a Proposed San Luis Drain Extension*, USGS report 00-416.

Maider, K. J. *et al.* (1993) Comparative Toxicity of Selenate, Selenite, Seleno-DL-methionine, and Seleno-DL-cysteine to *Daphia Magna*: *Environmental Toxicology and Chemistry*, v. 12, pp. 755-763.

Mosher, B. W. and Duce, R. A. (1983) *J. Geophys. Res.*, vol. 88, pp. 6761.

Mosher B. W. and Duce, R. A. (1989) The Atmosphere, in *Occurrence and Distribution of Selenium*, Ed. by Milan Ihnat, CRC Press, Inc. Florida, pp. 309.

(NIWQP) National Irrigation Water Quality Program (Department of the Interior), Information Report No. 3, *Guidelines for Interpretation of the Biological Effects of Selected Constituents in Biota, Water, and Sediment: Selenium*, November 1998.

Nriagu, J. O. (1989) Global Cycling of Selenium, in *Occurrence and Distribution of Selenium*, Ed. by Milan Ihnat, CRC Press, Inc. Florida, pp. 327-340.

(OCPFRD) Orange County Public Facilities and Resources Department (2000) September 1999 Peters Canyon Wash/San Diego Creek Nutrient Study.

Ogden Environmental and Energy Services (2000) Final Sampling and Analysis Plan for Newport Harbor Sediment Characterization.

(OEHHA) Office of Environmental Health Hazard Assessment (1999) Prevalence of Selected Target Chemical Contaminants in Sport Fish from Two California Lakes: Public Health Designed Screening Study. June 1999, Robert K. Brodberg, Ph.D. and Gerald A. Pollack, Ph.D. Pesticide and Environmental Toxicology Section, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, Sacramento, California.

Presser, T. S. (1994) Geologic Origin and Pathways of Selenium from the California Coast Ranges to the West-Central San Joaquin Valley, in *Selenium in the Environment*, Ed. by W. T. Frankenberger Jr. and Sally Benson, Marcel Dekker, Inc. New York, pp. 139-155.

Seiler, R. L. *et al.* (1999) Areas Susceptible to Irrigation-Induced Selenium Contamination of Water and Biota in the Western United States: US Geological Survey Circular 1180, pp. 36.

Skorupa, J. P (1998) Selenium Poisoning of Fish and Wildlife in Nature: Lessons from Twelve Real-World Examples, in *Environmental Chemistry of Selenium*, Ed. by W. T. Frankenberger Jr. and R. A. Engberg, Marcel Dekker, Inc.

Tokunaga, T. K. *et al.* (1994) Field Investigations of Selenium Speciation, Transformation, and Transport in Soils from Kesterson Reservoir and Lahontan Valley, in *Selenium in the Environment*, Ed. by W. T. Frankenberger Jr. and S. Benson, Marcel Dekker, Inc. Yew York, pp. 119-138.

TOXSCAN, Inc. (1995) Chemical Analysis and Toxicity Evaluation of Sediment Proposed for Dredging and Ocean Disposal: Unit I Sediment Basin and Access Channel.

(USEPA Region 9), United States Environmental Protection Agency (2000) Guidance for Developing TMDLs in California.

(USEPA) United States Environmental Protection Agency (2000) Water Quality standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California, 40 CFR Part 131.

(USFWS) United States Fish and Wildlife Services (2000) Biological Opinion on EPA's "Water Quality Standards: Establishment of Numeric Criteria for Priority Toxic Pollutants or the State of California".

Wang, W.-X. et al. (1996) Kinetic Determinations of Trace Element Bioaccumulation in the Mussel *Mytilus edulis*: *Marine Ecology: Progress Series*, vol. 140, pp. 91-113.

Wilber, C. G. (1980) Toxicology of Selenium: A Review, *Clin. Toxicol*., vol. 17, pp. 171, 1980.

APPENDIX A – Se Annual Load Calculation (IRWD's MONTHLY MONITORING DATA)

Computation Methodology

The following is the step-by-step procedure used in estimating the annual and seasonal selenium loads to Newport Bay.

a. Obtain IRWD's monthly data for selenium concentrations at Campus Drive in San Diego Creek from 12/97 to 3/99. An one-year window, 4/1/98 – 3/31/99, is selected for estimating annual load. Selenium load from 4/1/98 to 9/30/98 is termed dry season load and the rest (10/1/98 – 3/31/99) is wet season load. Annual load is then the combination of the dry season and wet season loads.

b. Obtain OCPFRD's daily flow record for the time period of analysis. The daily flow rates were summed up into dry season flow volume and wet season flow volume according to the time windows selected in step *a*.

c. Take natural log of the concentration data from step *a*.

d. Calculate means (μ) and variances (s^2) of the natural logs obtained from step *c* using statistical analysis tool imbedded in Microsfot, Excel.

e. Use the following formula to calculate expected values *ev* (also known as mean of the concentrations) for dry and wet seasons.

$$ev = e^{\left(\mu + \frac{s^2}{2}\right)}$$

Calculate upper and lower confidence limits, x_{hi} and x_{lo} from μ, *s*, and standardized normal deviate, *z*.

$$x_{hi} = e^{(\mu\ +\ zs)}, \qquad x_{lo} = e^{(\mu\ -\ zs)}$$

The value of *z* corresponds to a given probability of exceedence, which can be converted to a confidence level. For a confidence level of 90%, the *z* value corresponding to 0.90 is 1.28 (obtained from a standard normal distribution table).

f. Calculate expected selenium loads by multiplying the expected values (mean of concentrations) from step *e* by flow volumes from step *b* for both dry and wet seasons. Expected selenium loads are converted to pounds (lbs) using conversion factor 1 μg/L*cfs = 0.0054 lbs.

g. Repeat step *g* to obtain 90% confidence limits for expected selenium loads for dry and wet seasons by substituting the expected values with the confidence limits from step *f*.

Table A1. IRWD's monthly monitoring data and calculated daily load based on Orange County's flow data

Date	Flow (cfs)	Se Conc. (ug/L)	Daily Load (lbs/day)
12/18/97	411	27.8	61.63
01/17/98	13	22.3	1.56
02/19/98	88	36.86	17.50
03/10/98	32	64.99	11.22
04/16/98	21	64.57	7.31
05/21/98	21	23.68	2.68
06/16/98	13	38.12	2.67
07/07/98	11	40.49	2.40
08/12/98	15	33.82	2.74
09/01/98	13	30.72	2.15
10/27/98	17	43.74	4.01
11/18/98	237	49.61	63.42
12/15/98	9.1	36.87	1.81
01/07/99	13	36.97	2.59
02/23/99	14	42.59	3.22
03/30/99	9.4	52.91	2.68

Table A2. Calculations of seasonal and annual loads of selenium using IRWD's monitoring data and flow rate data.

Date	Conc. (ug/L)	ln(conc.)		Dry 4/1/98-9/30/98	Wet 10/1/98-3/31/99	Total 4/1/98-3/31/99
03/10/98	64.99	4.17				
04/16/98	64.57	4.17	**Mean**	3.60	3.77	
05/21/98	23.68	3.16	**Variance, *s2***	0.11	0.02	
06/16/98	38.12	3.64	***s***	0.33	0.15	
07/07/98	40.49	3.70	***ev***	38.84	43.86	
08/12/98	33.82	3.52	**Total flow (cfs)**	5852.50	8531.20	
09/01/98	30.72	3.42	**Load (lbs)**	1227.44	2020.59	3248.02
10/27/98	43.74	3.78				
11/18/98	49.61	3.90	***xhi* (90%)**	56.37	52.44	
12/15/98	36.87	3.61	***xlo* (90%)**	23.92	35.88	
01/07/99	36.97	3.61	**Load for *xhi* (lbs)**	1781.51	2416.05	
02/23/99	42.59	3.75	**Load for *xlo* (lbs)**	755.99	1653.13	
03/30/99	52.91	3.97				

Date	Flow (cfs)	Date	Flow (cfs)	Date	Flow (cfs)	Date	Flow (cfs)
03/01/98	88	04/20/98	22	06/09/98	20	07/29/98	18
03/02/98	75	04/21/98	22	06/10/98	19	07/30/98	15
03/03/98	80	04/22/98	22	06/11/98	32	07/31/98	16
03/04/98	65	04/23/98	22	06/12/98	45	08/01/98	15
03/05/98	37	04/24/98	22	06/13/98	21	08/02/98	15
03/06/98	38.5	04/25/98	22	06/14/98	18	08/03/98	14
03/07/98	40	04/26/98	21.5	06/15/98	17	08/04/98	15
03/08/98	34	04/27/98	21	06/16/98	19	08/05/98	14
03/09/98	33	04/28/98	21	06/17/98	21	08/06/98	15
03/10/98	31	04/29/98	22	06/18/98	19	08/07/98	16
03/11/98	31.5	04/30/98	23	06/19/98	18	08/08/98	16
03/12/98	32	05/01/98	20	06/20/98	19	08/09/98	16
03/13/98	114	05/02/98	21	06/21/98	15.5	08/10/98	15
03/14/98	465	05/03/98	21	06/22/98	12	08/11/98	15
03/15/98	42	05/04/98	24	06/23/98	16	08/12/98	16
03/16/98	39.5	05/05/98	484	06/24/98	13	08/13/98	15
03/17/98	37	05/06/98	255	06/25/98	13	08/14/98	16
03/18/98	33	05/07/98	26	06/26/98	13.5	08/15/98	14
03/19/98	31	05/08/98	26	06/27/98	14	08/16/98	13
03/20/98	32	05/09/98	19	06/28/98	13	08/17/98	14
03/21/98	31.5	05/10/98	17	06/29/98	14	08/18/98	13
03/22/98	31	05/11/98	233.5	06/30/98	12	08/19/98	14
03/23/98	26	05/12/98	450	07/01/98	12	08/20/98	12
03/24/98	24	05/13/98	678	07/02/98	9.4	08/21/98	15
03/25/98	1110	05/14/98	46	07/03/98	9.7	08/22/98	15
03/26/98	582.5	05/15/98	30	07/04/98	10	08/23/98	14
03/27/98	55	05/16/98	24.5	07/05/98	9.5	08/24/98	13
03/28/98	322	05/17/98	19	07/06/98	11	08/25/98	13
03/29/98	60	05/18/98	17	07/07/98	9.5	08/26/98	16
03/30/98	41	05/19/98	17	07/08/98	7.8	08/27/98	15
03/31/98	475	05/20/98	18	07/09/98	9.6	08/28/98	16
04/01/98	373	05/21/98	17.5	07/10/98	14	08/29/98	11
04/02/98	75	05/22/98	17	07/11/98	11	08/30/98	11
04/03/98	40	05/23/98	18	07/12/98	10	08/31/98	11
04/04/98	40	05/24/98	18	07/13/98	10	09/01/98	14
04/05/98	35	05/25/98	17	07/14/98	11	09/02/98	16
04/06/98	35.5	05/26/98	18	07/15/98	9.4	09/03/98	18
04/07/98	36	05/27/98	19	07/16/98	9.6	09/04/98	28
04/08/98	55	05/28/98	18	07/17/98	11	09/05/98	17
04/09/98	54	05/29/98	22	07/18/98	11	09/06/98	11
04/10/98	30	05/30/98	20	07/19/98	10	09/07/98	11
04/11/98	57.5	05/31/98	21	07/20/98	11	09/08/98	11
04/12/98	85	06/01/98	22	07/21/98	12	09/09/98	12
04/13/98	31	06/02/98	21	07/22/98	15	09/10/98	12
04/14/98	26	06/03/98	22	07/23/98	13	09/11/98	13
04/15/98	24	06/04/98	20	07/24/98	16	09/12/98	13
04/16/98	31.5	06/05/98	20	07/25/98	17	09/13/98	14
04/17/98	19	06/06/98	20.5	07/26/98	16	09/14/98	14
04/18/98	21	06/07/98	21	07/27/98	14	09/15/98	14
04/19/98	20	06/08/98	20	07/28/98	16	09/16/98	14

Date	Flow (cfs)	Date	Flow (cfs)	Date	Flow (cfs)	Date	Flow (cfs)
09/17/98	15	11/06/98	17	12/26/98	4.4	02/14/99	15
09/18/98	18	11/07/98	15	12/27/98	4.3	02/15/99	16
09/19/98	18	11/08/98	452	12/28/98	4.5	02/16/99	16
09/20/98	17	11/09/98	11	12/29/98	4.3	02/17/99	16
09/21/98	17	11/10/98	7.8	12/30/98	9.7	02/18/99	16
09/22/98	19	11/11/98	8.8	12/31/98	12	02/19/99	16
09/23/98	19	11/12/98	7.7	01/01/99	12	02/20/99	16
09/24/98	19	11/13/98	7.2	01/02/99	12	02/21/99	17
09/25/98	19	11/14/98	7.3	01/03/99	15	02/22/99	15
09/26/98	18	11/15/98	7.4	01/04/99	13	02/23/99	15
09/27/98	18	11/16/98	7.7	01/05/99	13	02/24/99	16
09/28/98	18	11/17/98	7.5	01/06/99	13	02/25/99	16
09/29/98	17	11/18/98	7.7	01/07/99	15	02/26/99	16
09/30/98	20	11/19/98	7.9	01/08/99	14	02/27/99	15
10/01/98	16	11/20/98	5.5	01/09/99	13	02/28/99	14
10/02/98	15	11/21/98	3.7	01/10/99	13	03/01/99	88
10/03/98	17	11/22/98	4	01/11/99	14	03/02/99	75
10/04/98	16	11/23/98	4.1	01/12/99	14	03/03/99	80
10/05/98	15	11/24/98	4.1	01/13/99	13	03/04/99	65
10/06/98	14	11/25/98	4.1	01/14/99	14	03/05/99	37
10/07/98	15	11/26/98	4	01/15/99	14	03/06/99	38.5
10/08/98	18	11/27/98	3.9	01/16/99	13	03/07/99	40
10/09/98	16	11/28/98	237	01/17/99	13	03/08/99	34
10/10/98	18	11/29/98	7.9	01/18/99	12	03/09/99	33
10/11/98	17	11/30/98	3.9	01/19/99	11	03/10/99	31
10/12/98	16	12/01/98	348	01/20/99	44	03/11/99	31.5
10/13/98	17	12/02/98	36	01/21/99	21	03/12/99	32
10/14/98	19	12/03/98	7.4	01/22/99	15	03/13/99	114
10/15/98	19	12/04/98	20	01/23/99	13	03/14/99	465
10/16/98	17	12/05/98	71	01/24/99	12	03/15/99	42
10/17/98	17	12/06/98	211	01/25/99	284	03/16/99	39.5
10/18/98	17	12/07/98	6.1	01/26/99	361	03/17/99	37
10/19/98	16	12/08/98	4.8	01/27/99	302	03/18/99	33
10/20/98	16	12/09/98	4	01/28/99	19	03/19/99	31
10/21/98	16	12/10/98	3.7	01/29/99	16	03/20/99	32
10/22/98	15	12/11/98	3.5	01/30/99	14	03/21/99	31.5
10/23/98	16	12/12/98	3.6	01/31/99	243	03/22/99	31
10/24/98	16	12/13/98	3.5	02/01/99	21	03/23/99	26
10/25/98	24	12/14/98	3.6	02/02/99	14	03/24/99	24
10/26/98	14	12/15/98	3.8	02/03/99	13	03/25/99	1110
10/27/98	13	12/16/98	3.9	02/04/99	28	03/26/99	582.5
10/28/98	14	12/17/98	3.9	02/05/99	58	03/27/99	55
10/29/98	13	12/18/98	4.1	02/06/99	16	03/28/99	322
10/30/98	13	12/19/98	14	02/07/99	14	03/29/99	60
10/31/98	12	12/20/98	24	02/08/99	13	03/30/99	41
11/01/98	13	12/21/98	5	02/09/99	38	03/31/99	475
11/02/98	13	12/22/98	5.1	02/10/99	35		
11/03/98	13	12/23/98	6.4	02/11/99	15		
11/04/98	13	12/24/98	8.8	02/12/99	14		
11/05/98	14	12/25/98	9.1	02/13/99	15		

APPENDIX B – SURFACE CHANNEL SELENIUM DATA 4/15/99 – 5/1/00 (HIBBS and LEE, 2000)

Table B1. Selenium concentrations in tributaries creeks and drains of San Diego Creek (Hibbs and Lee, 2000)

Sampling Location	Date	Conc. (ug/L)
Hicks Canyon Wash at concluence with Peters Canyon Wash	05/28/99	6
Central Irvine Channel at confluence with Peters Canyon Wash	05/28/99	11
El Modena Channel at Michelle Dr	04/15/99	<4
El Modena Channel at Michelle Dr	05/25/99	5
El Modena Channel at Michelle Dr	05/28/99	9
El Modena Channel at Michelle Dr	06/21/99	7
El Modena Chanel at confluence with Peters Canyon Wash	08/01/99	11
Como Channel at confluence with PCW	05/28/99	42
Como Channel at confluence with PCW	05/01/00	38
Santa Fe Channel at confluence with PCW	06/21/99	16
Santa Fe Channel at confluence with PCW	09/12/99	15
Santa Fe Channel at confluence with PCW	05/01/00	32
Circ. Drain at Irvine Center Dr at confluence with PCW	08/01/99	162
Circ. Drain at Irvine Center Dr at confluence with PCW	10/31/99	141
Valencia (Moffett) Drain at confluence with PCW	08/01/99	25
Valencia (Moffett) Drain at confluence with PCW	10/31/99	40
Warner Drain at confluence with Peters Canyon Wash	06/21/99	33
Warner Drain at confluence with Peters Canyon Wash	08/01/99	28
Warner Drain at confluence with Peters Canyon Wash	10/31/99	24
Circ. Drain at Barranca Pkwy at confluence with PCW	07/05/99	107
San Diego Creek at confluence with PCW	04/15/99	39
San Diego Creek at confluence with PCW	04/15/99	15
San Diego Creek at confluence with PCW	04/15/99	18
Barranca Channel at confluence with SDC	06/21/99	13
Barranca Channel at confluence with SDC	10/02/99	12
Lane Channel at confluence with SDC	07/05/99	25
Lane Channel at McCabe	10/02/99	21
Lane Channel at McCabe	11/08/99	18
San Joaquin Channel at confluence with SDC	07/05/99	11
San Joaquin Channel at confluence with SDC	10/31/99	9
Sand Canyon Wash at confluence with SDC	10/31/99	5
Bonita Canyon at confluence with SDC	07/05/99	14
Santa Ana Delhi Channel at Irvine Ave	07/05/99	18
San Diego Creek at Campus Dr	10/31/99	19

Table B2. Selenium load from groundwater in three drainage channels based on upstream and downstream flow and selenium concentration measurements.

Channel	**Date**	**Upstream**		**Downstream**		**Load from groundwater**
		Flow (cfs)	Conc. (μg/L)	Flow (cfs)	Conc. (μg/L)	(lb/day)
San Diego Creek Reach 2	08/28/99	1.63	4	2.32	18	0.19
Como Channel	05/01/00	0.0004	<4	0.44	38	0.09
Santa Fe Channel	05/01/00	0.019	<4	0.46	32	0.08

Note: Daily loads of selenium from groundwater are calculated by the differences in loads between downstream and upstream.

APPENDIX C – 319h TOXICITY SOURCE STUDY
1/25/00 – 5/31/00 (LEE *et al.*, 2001)

Station	01/25/00		02/12/00		02/21/00		05/31/00		Land Use (%)			
	total	dissolved	total	dissolved	total	dissolved	total	dissolved	Area (acres)	Urban	Open Space	Ag.
1. San Diego Creek @ Campus	15.6	13.4	7.4	4	5.4	3.3	22.1	23	76,200	67	23	10
2. San Diego Creek @ Harvard			5.2	1.9	5.4	2	10.1	9.2	27,000	51	36	13
3. Peters Canyon @ Barranca			11.7	9.3	8.2	6.5	31	30.2	29,000	64	15	21
4. Hines Channel @ Irvine Blvd.			26.5	20.2	20	18.4	2.9	3.3	620	4	1	95
5. San Joaquin @ University Dr.			3.96	4.6	3.6	3.4			890	----	10	90
6. Santa Ana-Delhi @ Mesa Dr.			<0.39	2.9	3.4	0.92	11.9	11.5	11,000	92	6	2
7. Peters Canyon Wash @ Walnut Ave.			11.6	9.7					12,700	30	25	45
8. El Modena - Irvine Channel Upstream of Peters Canyon					3.2	2.6	12.2	12.1	7,700	96	----	4
9. Sand Canyon Channel @ Irvine Blvd			24.8	26.9	20.5	16.5			101	----	----	100
10. East Costa Mesa Channel @ Highland Ave.			4	1	0.82	0.54	2.7	2.8	870	100	----	----
11. Irvine Central Channel @ Monroe			13.9	11.8	6.7	6.1	33.5	36.2	2,200	29	----	71

California Regional Water Quality Control Board
Santa Ana Region

Diazinon and Chlorpyrifos TMDL for Upper Newport Bay and San Diego Creek

Draft
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1.0 PROBLEM STATEMENT

1.1 INTRODUCTION

An investigation of stormwater runoff in tributaries to Newport Bay in 1992 and 1993 demonstrated the existence of aquatic life toxicity (Bailey et al, 1993). A toxicity identification evaluation (TIE) performed on several of the samples collected during the study, indicated that one or more pesticides were responsible for the observed toxicity, and that diazinon was likely one of these pesticides.

Separate sampling programs, the Toxic Substances Monitoring (TSM) program, and the State Mussel Watch (SMW), demonstrated that chlorpyrifos and diazinon were present in fish and mussel tissue. The TSM and SMW were conducted in upper and lower Newport Bay as well as in the drainage channels in the Newport Bay watershed, with diazinon and chlorpyrifos data available from 1983 onwards.

As a result of these investigations, pesticides were included on the 1998 California 303d list for upper and lower Newport Bay, and for Reach 1 of San Diego Creek. Reach 2 of San Diego Creek was listed for unknown toxicity.

Supplemental studies to determine the sources of the toxicity observed during the 1992-93 investigation were carried out from 1996 to 2000 (Lee and Taylor, 1999, 2001). These studies further documented the occurrence of aquatic life toxicity in the Newport Bay watershed, and concluded that diazinon and chlorpyrifos were causing a large portion of the observed toxicity in San Diego Creek. An investigation of Upper Newport Bay indicated the presence of toxicity attributable to chlorpyrifos in stormwater runoff entering the upper bay from San Diego Creek. There were no samples collected from lower Newport Bay.

Based on these findings, TMDL development for diazinon and chlorpyrifos in San Diego Creek, and chlorpyrifos in upper Newport Bay was initiated (Santa Ana Regional Water Quality Control Board [SARWQCB], January 2001). Diazinon and chlorpyrifos are widely used organophosphate pesticides, and are among the pesticides detected most frequently in urban waterways. Further details on diazinon and chlorpyrifos usage in the Newport Bay watershed can be found in **Section 3**.

The remainder of this problem statement summarizes previous investigations in the Newport Bay watershed and describes the impairment of water quality standards caused by pesticide-derived aquatic life toxicity.

1.2 PREVIOUS INVESTIGATIONS/AVAILABLE DATA

This TMDL is based on analysis of data collected in the Newport Bay watershed over the past five years. The available data were generated by state and local agencies as part of various investigative or monitoring programs. These programs are briefly described below.

1. <u>Toxic Substances Monitoring (TSM) and State Mussel Watch (SMW)</u>: The TSM and SMW are statewide screening programs designed to identify areas where toxic substances are bioaccumulating in fish and mussel tissue. The TSM program includes four locations in the

Newport Bay watershed, one location in Upper Newport Bay, and one location in Lower Newport Bay. Samples analyzed for diazinon and chlorpyrifos have been collected beginning in 1983, and has continued at irregular intervals through 2000. The SMW program has collected samples for diazinon and chlorpyrifos analysis from 19 locations, mostly within Upper and Lower Newport Bay. Although some of the locations were sampled only once or twice since 1982, annual samples have been collected at several locations for over ten years.

2. Aquatic Life Toxicity Investigations; 319(h) and 205(j) studies: Studies of stormwater runoff in tributaries to Newport Bay in 1992 and 1993 demonstrated the existence of aquatic life toxicity. As a result, supplemental studies to determine the sources of the observed toxicity were carried out from 1996 to 2000. These studies were funded under the USEPA Clean Water Act Section 205j and 319h grant programs. The first study, (under the 205j program) was carried out from 1996-1999. Eighty-five samples were collected from seven stormwater runoff events and four dry-weather sampling events. The second study (under the 319h program) was carried out during 1999 and 2000. Three stormwater runoff events, and two dry weather events were monitored, and a total of 31 samples were analyzed for diazinon and chlorpyrifos. Further details on these studies can be found in the respective reports (Lee and Taylor, 1999; 2001).

3. Orange County Public Facilities and Resources Department (OCPFRD): Orange County has been implementing a water quality monitoring program since 1991 as part of its NPDES permit. Although no diazinon and chlorpyrifos analyses are currently required under this permit, the OCPFRD has collected semi-annual sediment data for diazinon analysis.

3. California Department of Pesticide Regulation (CDPR) Pesticide Use Reports: Beginning in January 1990, California required growers to report all pesticides used on all crops. All pesticides applied on golf courses, parks, cemeteries, rangeland, pasture, and along roadside and railroad rights-of-way were also subject to the expanded reporting requirements. Pesticide dealers also faced expanded reporting and record keeping requirements. Structural fumigators, professional gardeners and other nonagricultural Pest Control Operators continued to report all pesticide use. Home-use pesticides are exempt from the regulations.

4. CDPR Red Imported Fire Ant (RIFA) Monitoring: The RIFA is an aggressive, exotic insect that was first discovered in Southern California in October 1998. In response, the California Department of Food and Agriculture (CDFA) designed a RIFA eradication/control plan to deal with the infestations (CDFA, March 1999). Part of the plan required treatment of targeted areas with a suite of pesticides that included diazinon and chlorpyrifos.

To monitor the environmental impact of the RIFA plan, a surface water sampling program was initiated in Orange County, conducted by the CDPR. Over 100 samples were collected and analyzed for pesticides during the period March/April 1999 to January 2001. These included 22 rounds of monthly sampling and one rainfall runoff sampling event. Data from the sampling events are summarized in monthly monitoring memos (CDPR, 1999-2000).

5. CDPR Sales and Use Survey: The CDPR and the University of California conducted a residential pesticide survey to better document the residential use occurring in the Newport Bay watershed. Preliminary results from the survey are available, however, the project is not scheduled for completion until December 2001.

1.3 WATER QUALITY STANDARDS

Beneficial Uses: Beneficial Uses for San Diego Creek are designated in the Basin Plan (SARWQCB, 1995). San Diego Creek Reach 1 has the designated beneficial uses of water contact recreation (REC1), non-contact water recreation (REC2), warm freshwater habitat (WARM), and wildlife habitat (WILD). Reach 2 is listed for the same uses but is deemed to possess these beneficial uses only intermittently. In addition, Reach 2 has the intermittent groundwater recharge (GWR) beneficial use designation (SARWQCB, 1995).

Upper Newport Bay has the REC1, REC2, and WILD designated beneficial uses, as well as the following seven additional beneficial uses:

- Preservation of Biological Habitats of Special Significance (BIOL)
- Commercial and Sport Fishing (COMM)
- Estuarine Habitat (EST)
- Marine Habitat (MAR)
- Rare, Threatened, or Endangered Species (RARE)
- Spawning, Reproduction, and Development (SPWN)
- Shellfish Harvesting (SHEL)

Numeric Water Quality Objectives: The Regional Board has not adopted numeric water quality objectives for diazinon and chlorpyrifos. The USEPA has promulgated numeric water quality criteria for California for priority toxic pollutants, but diazinon and chlorpyrifos are not included in this list.

Narrative Water Quality Objectives: The Basin Plan specifies two narrative water quality objectives for toxic substances. These are:

(1) *Toxic substance shall not be discharged at levels that will bioaccumulate in aquatic resources to levels which are harmful to human health*, and
(2) *The concentration of toxic substances in the water column, sediment or biota shall not adversely affect beneficial uses*.

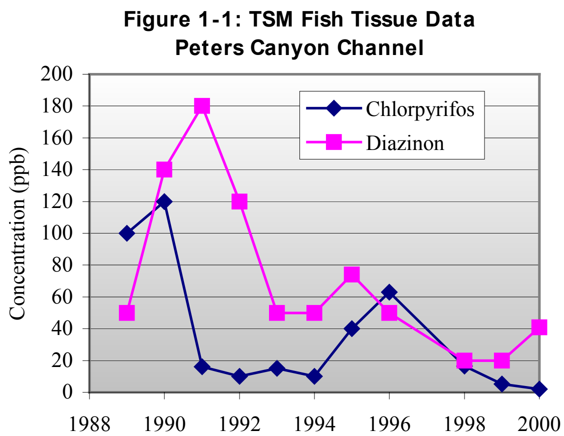
Antidegradation Standard: As diazinon and chlorpyrifos are man-made chemicals that do not naturally occur in the environment, it can be argued that their presence in a surface water constitutes a lowering of the water quality of that surface water. This is permissible only if beneficial uses are protected, and the lowering of water quality is consistent with the maximum benefit to the people of the state of California.

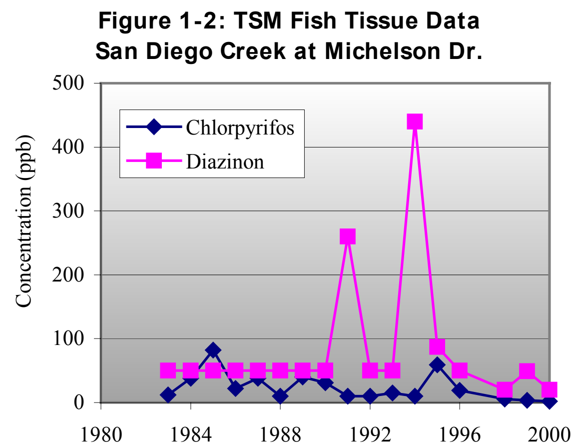
1.4 IMPAIRMENT ASSESSMENT

1.4.1 Bioaccumulation and Food Consumption Guidelines/Limits

The TSM and SMW programs have collected fish, mussel, and tissue samples from the Newport Bay watershed. Samples have been collected from within both Upper and Lower Newport Bay, and from San Diego Creek and its tributaries.

TSM data: Chlorpyrifos concentrations have consistently remained orders-of-magnitude below the OEHHA screening value (10,000 ppb) for fish consumption. Diazinon concentrations have exceeded the OEHHA screening value of 300 ppb only once (440 ug/kg) during the programs history. **Figures 1-1 and 1-2** show the TSM results for the two stations where the longest record of data is available (Peters Canyon Channel and San Diego Creek at Michelson), and where the highest diazinon concentration was observed.





(OEHHA Screening Values: Diazinon = 300 ppb; Chlorpyrifos = 10,000 ppb)

SMW data: Diazinon and chlorpyrifos concentrations in mussel tissue have never exceeded the OEHHA guidelines. The observed concentrations were only detected intermittently and there is no trend apparent in the data. Detection frequencies were 40% and less than 10% for chlorpyrifos and diazinon respectively.

Bioaccumulation

Diazinon and chlorpyrifos are not known to bioaccumulate to levels of concern in the environment. The bioaccumulation factor (BAF) for diazinon in fish is generally less than 100 (L/kg). Although diazinon and chlorpyrifos are detected intermittently in the TSM and SMW programs, the concentrations observed in the Newport Bay watershed do not provide evidence of bioaccumulation. Rough bioaccumulation factors calculated using the TSM fish data and water column concentration data collected in the Newport Bay watershed from 1996-2001, are about 54 for diazinon and 32 for chlorpyrifos (L/kg). Bioaccumulative chemicals of concern are generally those that have BAFs greater than 1,000.

1.4.2 Aquatic Life Toxicity

San Diego Creek and Upper Newport Bay were listed as impaired due in part to pesticide-derived toxicity (303d). Although a mixture of pesticides was associated with the toxicity, the primary sources of toxicity were identified as diazinon and chlorpyrifos. The impairment was documented through over 300 acute toxicity tests conducted on 123 water samples from 1996 to 2001. The toxicity tests were performed as part of the 205j and 319h programs, and as part of the DPR-RIFA water quality investigation. In addition, nurseries in the Newport Bay watershed that have waste discharge permits began conducting bimonthly chronic toxicity tests in 2000.

Figures 1-3 and **1-4** summarize the toxicity test results using *Ceriodaphnia dubia*, (the most sensitive of the test species). Eighty-one toxicity tests were conducted on baseflow samples collected in the Newport Bay watershed. Toxicity to *Ceriodaphnia* was not present in 20% of these tests, while 80% of the tests resulted in at least partial mortality to *Ceriodaphnia* (**Figure 1-3**).

Figure 1-3: Ceriodaphnia Toxicity Tests in the Newport Bay Watershed
Baseflow; 1996-2001

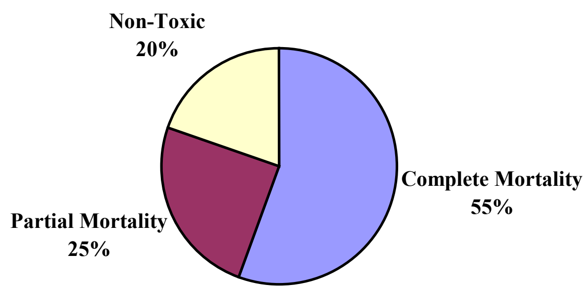
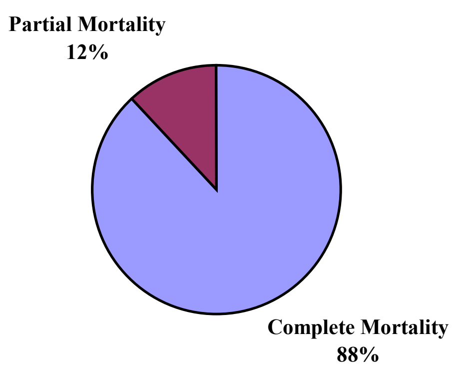


Figure 1-4 summarizes the stormwater toxicity data. Forty-two toxicity tests were conducted on stormwater samples collected from various locations in the Newport Bay watershed. All samples were toxic to *Ceriodaphnia*, with 88% of the samples causing complete mortality within a few days.

Figure 1-4: Ceriodaphnia Toxicity Tests in the Newport Bay Watershed
Stormflow; 1996-2001



Aquatic Life Toxicity Investigations (319h and 205j Programs):
A total of 63 undiluted samples were collected for acute toxicity testing during the 205j and 319h investigations. Several additional samples required dilution prior to testing due to salinity levels that were high enough to cause mortality to one of the test organisms *(Ceriodaphnia dubia)*. Serial dilutions and TIE procedures resulted in over 300 toxicity tests being conducted on the water samples.

Toxicity attributable to diazinon and chlorpyrifos occurred in San Diego Creek during virtually all monitored storm events. Dry weather toxicity was generally confined to the upper reaches of the watershed and diluted or otherwise ameliorated upstream of monitoring locations in San Diego Creek. (Lee and Taylor, 1999, 2001) In the 319h study, 100% *Ceriodaphnia* mortality was observed in virtually all storm samples, usually within 2 days. Stormwater runoff samples, with the salinity adjusted to that of seawater, were also toxic to the saltwater test species *Mysidopsis bahia*. The toxicity to *Mysidopsis* is attributable to the chlorpyrifos concentration in the samples.

Most of the toxicity tests performed under the 319h program were supplemented with serial dilutions to measure the acute toxic units present. TIEs were also performed in many cases to identify the specific constituents responsible for the observed toxicity.

Table 1-1 shows toxicity test data on samples collected in the Newport Bay watershed during the 319h investigation. The data are sorted by the expected toxicity based on the water column concentrations, and reference LC50s for diazinon and chlorpyrifos. The LC50 is the concentration of a toxic constituent that results in 50% mortality to the test organism. For **Table 1-1**, the reference LC50s are those published by the CDDFG (CDFG 2000a: diazinon = 440 ng/L and chlorpyrifos = 60 ng/L). Measured toxicity that exceeds the expected toxicity indicates the presence of additional compounds at toxic concentrations. Based on TIE work performed on these samples, the additional toxicity is mainly attributable to carbaryl, and potentially to some pyrethroid pesticides. Several samples still had significant toxicity that was due to unknown causes.

Table 1-1: Results of 319h *Ceriodapahnia* Acute Toxicity Tests
(sorted by expected diazion and chlorpyrifos toxicity)

		GC Results (ng/L)		Mortality		Acute Toxicity (TUa)	
Station	Date	Chlorpyrifos	Diazinon	(%)	(days)	Measured	Expected
San Joaquin Creek – Univ Dr.	12-Feb-00	770	<50	100	1	32	12.8
San Joaquin Creek – Univ Dr.	21-Feb-00	470	<50	100	1	6	7.8
San Diego Creek - Harvard Av.	12-Feb-00	310	280	100	1	8	5.8
Hines Channel - Irvine Blvd.	29-Sep-99	310	220	100	1	16	5.7
San Diego Creek - Campus Dr.	12-Feb-00	260	460	100	1	8	5.4
Central Irvine Channel - Monroe	12-Feb-00	150	810	100	1	8	4.3
Hines Channel - Irvine Blvd.	12-Feb-00	120	760	100	1	8	3.7
Peters Canyon Channel - Walnut	12-Feb-00	150	520	100	1	16	3.7
San Diego Creek - Harvard Av.	21-Feb-00	190	200	100	1	3	3.6
San Diego Creek - Campus Dr.	25-Jan-00	160	320	100	1	8	3.4
San Diego Creek - Campus Dr.	21-Feb-00	170	220	100	1	5	3.3
Hines Channel - Irvine Blvd.	21-Feb-00	50	810	100	1	5	2.7
Peters Canyon - Barranca	12-Feb-00	100	420	100	1	8	2.6
Peters Canyon - Barranca	21-Feb-00	80	330	100	1	3	2.1
Peters Canyon - Barranca	29-Sep-99	<50	820	100	1	2	1.9
Central Irvine Channel - Monroe	21-Feb-00	70	280	100	1	5.5	1.8
East Costa Mesa - Highland Dr.	12-Feb-00	<50	370	100	2	n/a	1.7
East Costa Mesa - Highland Dr.	21-Feb-00	<50	560	100	1	2.5	1.3
El Modena-Irvine upstream of PCC	21-Feb-00	<50	330	100	6	0	0.8
East Costa Mesa - Highland Dr.	31-May-00	<50	210	100	5	1	0.5
Santa Ana Delhi - Mesa Dr.	21-Feb-00	<50	200	100	7	0	0.5
El Modena-Irvine upstream of PCC	31-May-00	<50	180	0	0	0	0.4
Peters Canyon – Barranca	31-May-00	<50	170	0	0	0	0.4
San Diego Creek - Campus Dr.	31-May-00	<50	160	0	0	0	0.4
Santa Ana Delhi - Mesa Dr.	12-Feb-00	<50	120	100	3	1	0.3
Santa Ana Delhi - Mesa Dr.	31-May-00	<50	110	0	0	0	0.3
Sand Canyon Ave - NE corner Irv. Blvd.	12-Feb-00	<50	110	22	7	0	0.3
Central Irvine Channel - Monroe	31-May-00	<50	90	n/a	n/a	n/a	0.2
Sand Canyon Ave - NE corner Irv. Blvd.	21-Feb-00	<50	70	30	7	0	0.2
Hines Channel - Irvine Blvd.	31-May-00	<50	47	44	7	n/a	0.1
San Diego Creek - Harvard Av.	31-May-00	<50	<50	0	0	0	0.0

n/a = not available; TUa = acute toxic units
(Adapted from Lee and Taylor,2001)

DPR-RIFA: Acute Toxicity Tests
The DPR has completed 22 sampling rounds in the Newport Bay watershed. Sixty acute toxicity tests have been performed using *Ceriodaphnia dubia*. The DPR-RIFA tests were not accompanied by serial dilutions or TIEs, and identification of the toxic constituents was based on expected toxicity derived from reference LC50 data.

The DPR has not completed detailed data analysis for the RIFA monitoring project, however, preliminary data indicate that chlorpyrifos and diazinon are responsible for most of the observed toxicity in San Diego Creek. At the nursery discharge monitoring locations, bifenthrin appears to account for a significant portion of the toxicity in addition to diazinon, and chlorpyrifos. However, bifenthrin is relatively immobile compared to diazinon and chlorpyrifos, and has been detected in only one of 22 DPR monthly sampling events in San Diego Creek (CDPR, 1999-2001).

Nurseries: Chronic Toxicity Tests
The nurseries in the Newport Bay watershed began performing chronic toxicity tests on their effluent in 2000 to comply with new Waste Discharge Requirements that were being implemented for the nutrient TMDL. As of January 2001, Hines Nurseries had completed seven chronic toxicity tests, and El Modeno Gardens had completed two chronic toxicity tests. Bordiers Nursery had not yet conducted chronic toxicity tests.

Test results were generally 2 chronic toxic units (TUc) for reproduction and 1-2 TUc for survival. Constituents responsible for the observed chronic toxicity are not currently identified through additional sampling and analysis. DPR data show that the mix of pesticides causing toxicity in nursery discharge typically includes diazinon, chlorpyrifos, and bifenthrin (CDPR, 1999-2001).

1.5 SUMMARY

Over 300 toxicity tests have been performed on 123 water samples collected from the Newport Bay watershed. These tests have demonstrated the persistent occurrence of aquatic life toxicity in San Diego Creek and its tributaries, and in Upper Newport Bay, particularly during storm events. Based on water column chemistry data and TIEs, there is conclusive evidence that diazinon and chlorpyrifos are causing acute and chronic toxicity in San Diego Creek and Upper Newport Bay (chlorpyrifos). There is no compelling evidence of bioaccumulation of these substances to levels of concern.

The persistent occurrence of aquatic life toxicity in San Diego Creek and Upper Newport Bay is a threat to the established beneficial uses of these waterbodies. Adverse impacts to these beneficial uses is a violation of the second narrative objective specified in the Basin Plan (SARWQCB, 1995).

2.0 NUMERIC TARGET

2.1 POTENTIAL NUMERIC TARGETS

Two methods have been proposed for setting numeric targets in the upper Newport Bay watershed. These are:

(1) The CDFG water quality criteria for diazinon and chlorpyrifos derived using USEPA guidelines (USEPA, 1985). Note these criteria have not been formally adopted, but are the best scientifically-derived guidance available.
(2) A Probabilistic Ecological Risk Assessment (PERA) for diazinon implemented by Novartis (Hall and Anderson, 2000). This method could also be applied for chlorpyrifos.

Tables 2-1 and **2-2** show potential diazinon and chlorpyrifos concentration targets, along with several reference concentrations for comparison.

Table 2-1 Potential Diazinon Target Concentrations and Reference Values (Freshwater)

Source	Concentration (ng/L)
California Department of Fish and Game (CDFG): CCC	50
CDFG: CMC	80
Probabilistic Ecological Risk Assessment (PERA): Arthropods 5th percentile	144
Reference :	
Ceriodaphnia LC50 (CDFG)	440
San Diego Creek stormwater average	445
San Diego Creek maximum	960

CCC=Criterion Continuous Concentration (chronic); CMC=Criterion Maximum Concentration (acute)

Table 2-2 Potential Chlorpyrifos Concentration Limits and Reference Values

Source	Concentration (ng/L)	
	Freshwater	Saltwater
California Department of Fish and Game (CDFG): CCC	14	9
CDFG: CMC	20	20
Reference :		
Ceriodaphnia LC50 or EC50 (CDFG)	60	---
Mysidopsis LC50 or EC50 (CDFG)	---	40
San Diego Creek Stormwater Average	87	---
San Diego Creek Maximum	580	---
Upper Newport Bay Average	---	43.3
Upper Newport Bay Maximum	---	132

CCC=Criterion Continuous Concentration (chronic); CMC=Criterion Maximum Concentration (acute)

<u>USEPA Method as Applied by CDFG</u>: The USEPA method provides for development of an acute and a chronic concentration criterion. The acute criterion is referred to as the Criterion

Maximum Concentration (CMC), and the chronic criterion is referred to as the Criterion Continuous Concentration. The use of two limits is intended to be less restrictive than "a one-number criterion would have to be in order to provide the same degree of protection" (USEPA, 1985).

The CMC is designed to "estimate the highest one-hour average concentration that should not result in unacceptable effects on aquatic organisms and their uses." The CCC is designed to "estimate the highest four-day average concentration that should not cause unacceptable toxicity during a long-term exposure" (USEPA, 1985).

The frequency of allowed exceedance for both the CCC and CMC is set as once in three years; an interval deemed sufficient to allow ecosystems to recover from the stress caused by the exceedance. The CCC and CMC are intended to provide protection to 95% of the species in the data set, and are derived by using acceptable toxicity tests from a representative set of species.

The methodology includes provisions to account for bioaccumulation, and for toxicity to plant species if warranted. As discussed in **Section 1.4.1**, bioaccumulation is not a concern for diazinon and chlorpyrifos. Toxicity to aquatic plants is also not a significant concern, based on toxicity test results in the Newport Bay watershed using the algae *Selenastrum capricornatum*.

PERA Method: The PERA is a risk assessment, and is more comprehensive in scope. The PERA approach characterizes risk to aquatic species by comparing distributions of environmental exposure data with distributions of species response data (toxicity data) from laboratory studies. The overlap of these distributions is a measure of potential risk to aquatic life.

The numeric target for the PERA is derived by pooling available toxicity tests to form a cumulative frequency distribution. The desired level of protection is then selected by choosing appropriate percentiles from the distribution (usually the 5th or 10th percentiles). In the Newport Bay watershed PERA, performed by Novartis (Hall and Anderson, September 2000) the 5th and 10th percentiles were determined separately for the entire toxicity data set (all species) and for arthropods (the most sensitive phylum to diazinon). The 5th percentile for arthropods corresponds to protection of 95% of arthropod species, and is similar to the USEPA acute criterion, which is designed to be protective of 95% of the species included in the representative data set.

Differences between the USEPA method and the PERA as implemented by Novartis include differing statistical methods for grouping and averaging the data, and the additional requirement in the USEPA method for selection of a representative set of taxa.

However, the major difference between the USEPA method and the PERA is the inclusion of a safety margin in the USEPA method. Although both methodologies are based on statistically determining the 5th percentile of the toxicity test data, the USEPA method includes a final step to divide the 5th percentile value by a factor of two. The rationale for this safety margin is that the toxicity test data are based on LC50s. Using the LC50 without the safety margin implies a numeric target that allows 50% mortality (or greater) at the selected level of protection (5th percentile). But as stated by USEPA, "a concentration that would severely harm 50% of the 5th percentile cannot be considered to be protective of that percentile or that species" (USEPA, 1985). Noting this point, USEPA Region IX has stated that the PERA method as implemented by Novartis, is not considered protective under the Clean Water Act (USEPA, August 2000a).

2.2 SELECTED TARGET

The CDFG applied the USEPA methodology by assembling a database of available toxicity tests and evaluating each test for inclusion in the set of tests used for calculating the acute and chronic recommended criteria. The selected numeric targets are the recommended acute and chronic criteria derived by the CDFG (CDFG 2000a). These concentrations are shown in **Table 2-3**. Setting numeric targets at the CDFG-derived criteria will ensure that aquatic organisms and their uses should not be affected unacceptably if the four-day average concentrations do not exceed the chronic numeric targets (**Table 2-3)**, more than once every three years on the average, and if the one-hour average concentrations do not exceed the acute numeric targets (**Table 2-3)** more than once every three years on the average.

Table 2-3 Selected Numeric Targets

		Concentration (ng/L)	
Pesticide	**Criterion**	**Freshwater**	**Saltwater**
Diazinon	Chronic (CCC)	50	---
Diazinon	Acute (CMC)	80	---
Chlorpyrifos	Chronic (CCC)	14	9
Chlorpyrifos	Acute (CMC)	20	20

CCC=Criterion Continuous Concentration;
CMC=Criterion Maximum Concentration

3.0 SOURCE ANALYSIS

3.1 INTRODUCTION

This section of the TMDL presents an analysis of the major sources of diazinon and chlorpyrifos to San Diego Creek and Upper Newport Bay. The source analysis focuses on water column concentrations, as these were associated with aquatic life toxicity and impairment of beneficial uses in San Diego Creek and Upper Newport Bay. Several investigations have been conducted in the watershed targeting aquatic life toxicity associated with pesticides. These studies were not detailed enough to identify discrete sources, but it is largely recognized that diazinon and chlorpyrifos are nonpoint source problems, and characterization of discrete sources throughout the watershed is impractical.

A source analysis approach based on correlating land use types with diazinon and chlorpyrifos export rates was employed in the 319h study (Lee and Taylor, 2001), however, this approach was hampered by the mixed land use patterns upstream of many of the sampling locations, and the limited number of samples. A study conducted by Scanlin and Feng (1997), suggested that diazinon loads could not be predicted on the basis of general land cover variables. Nevertheless, by pooling data from the various studies conducted in the watershed, estimates of chlorpyrifos and diazinon runoff concentrations and loads can be made according to broad land use categories.

The following sections analyze usage of chlorpyrifos and diazinon (Section 3.2). Environmental fate and transport parameters are discussed in Section 3.3. Section 3.4 presents a summary of the chlorpyrifos and diazinon data collected in the Newport Bay watershed and discusses the potential sources. Calculated load estimates are presented in Section 3.5. Conclusions are summarized in Section 3.6.

3.2 USAGE

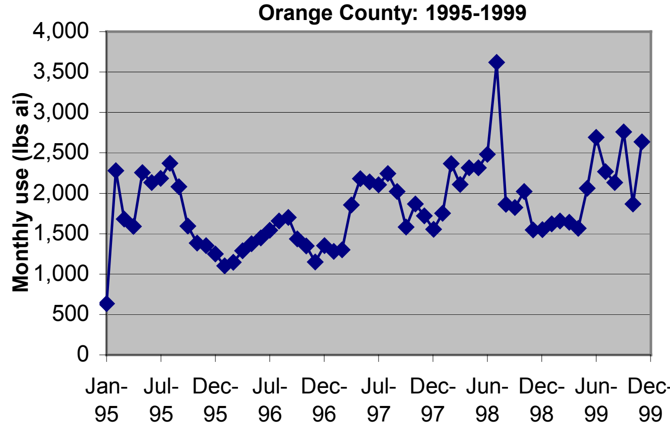
The CDPR requires records of all pesticide applications except for residential use by homeowners. These records are compiled and reported on a county-by-county basis. The Newport Bay watershed occupies 20% of Orange County, and it is assumed here that 20% of the pesticide use reported for Orange County occurred within the Newport Bay watershed.

3.2.1 Diazinon

As shown in **Figure 3-1**, reported diazinon use in Orange County has remained fairly steady over the past five years. Seasonally-correlated increases in diazinon use are apparent in the summer months in response to increased pest activity.

As noted above, residential use by homeowners is not reported in the CDPR database. Information on national pesticide usage by homeowners is available from the USEPA Pesticide Industry Sales and Usage Market Estimates report. On a national basis, 75% of the diazinon used in the US each year is for non-agricultural purposes, with 39% used by homeowners outdoors and 3% used by homeowners indoors (USEPA, November 1999). Total homeowner use is therefore about 42% on a national basis.

Fig 3-1: Reported Diazinon Use
Orange County: 1995-1999



In Orange County, the total agricultural use is likely less than the national average due to urbanization of the watershed. Thus homeowner uses probably account for more than the 42% reported nationally. A more specific estimate of the unreported homeowner use can be obtained by assuming the national ratio of homeowner use to total non-agricultural use (42/75, or 56%) is applicable to Orange County. Since data on the total non-agricultural diazinon use in Orange County is reported to the CDPR on a yearly basis, the national ratio can be used to estimate the unreported homeowner use in Orange County. Estimating the unreported homeowner use at 56% of total non-agricultural use results in a figure of 29,119 lbs active ingredient (ai) for 1999. This would amount to 54% of total use (including agricultural use) in Orange County; somewhat higher than the national figure of 42% reported by USEPA.

Tables 3-1 and 3-2 present the reported and estimated unreported diazinon use in Orange County. For 1999, the total diazinon use in the Newport Bay watershed would be one-fifth of the Orange County total, or approximately 10,714 lbs ai, while the estimated residential use would be about 5,824 lbs ai.

Table 3-2 indicates that urban uses accounted for over 97% of diazinon use, while agricultural uses (including nurseries) accounted for the remainder. Preliminary data from the Sales and Use Survey in the Newport Bay watershed (Wilen, forthcoming) indicate that unreported residential diazinon use in 2000 was about 7,864 lbs ai; about 32% larger than the estimate of 5,919 lbs presented above using separate national data. This would suggest that total urban uses account for more than the 97% indicated in **Table 3-2**.

Table 3-1: Reported and Estimated Unreported Diazinon Use
Orange County: 1995-1999 (lbs ai)

Use	1995	1996	1997	1998	1999
Structural	17,463	14,046	18,892	23,076	22,085
Nursery	1,037	839	803	1,212	1,144
Agriculture	2,004	746	1,363	865	429
Landscape	1,030	762	595	612	789
Other non-residential	9.8	46.2	1.6	1.7	5.3
Reported subtotal	21,543	16,439	21,655	25,766	24,452
Estimated Unreported Residential Use	23,548	18,905	24,804	30,150	29,119
Total	45,092	35,344	46,458	55,915	53,571

ai = active ingredient

Tables 3-1 and 3-2 show a decline in agriculture use from 1995 to 1999, both in absolute and percentage terms. The land use data also show a similar pattern, and the decline in agricultural diazinon usage may be a reflection of the continuing conversion of agricultural land to urban uses in Orange County and the Newport Bay watershed.

Table 3-2: Reported and Estimated Diazinon Use
Orange County: 1995-1999 (percent)

Use	1995	1996	1997	1998	1999
Structural	38.7%	39.7%	40.7%	41.3%	41.2%
Nursery	2.3%	2.4%	1.7%	2.2%	2.1%
Agriculture	4.4%	2.1%	2.9%	1.5%	0.8%
Landscape	2.3%	2.2%	1.3%	1.1%	1.5%
Other non-residential	0.0%	0.1%	0.0%	0.0%	0.0%
Estimated Residential	52%	53%	53%	54%	54%
Total	100%	100%	100%	100%	100%

USEPA Phaseout of Certain Diazinon Uses: In January 2001, USEPA released a revised risk assessment and an agreement with registrants to phase out most diazinon uses (USEPA, January 2001). Under the agreement, all indoor uses will be terminated, and all outdoor non-agricultural uses will be phased out over the next few years. Retail sales will be banned after December 31, 2002. The EPA expects that these actions will end about 75% of the current use of diazinon. In addition, about one-third of the agricultural crop uses will be removed.

The usage data in **Table 3-2** show that non-agricultural and non-nursery uses account for over 90% of the diazinon use in Orange County. It is thus likely that the EPA agreement will result in the cessation of most diazinon use in the Newport Bay watershed soon after the outdoor non-agricultural use registration expires on December 31, 2004.

3.2.2 Chlorpyrifos

Fig 3-2: Reported Chlorpyrifos Use
Orange County: 1995-1999

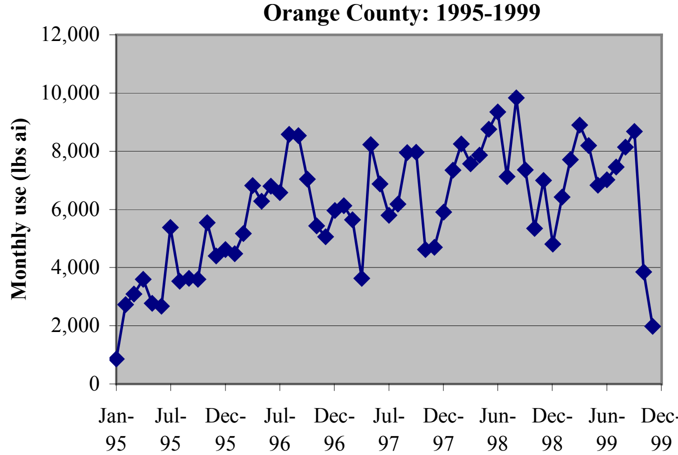


Figure 3-2 shows the reported Chlorpyrifos use in Orange County from 1995 to 1999. As with diazinon, higher use tends to occur in the dry season, and is likely correlated with increased pest activity during warmer weather. An increasing trend from 1995 to 1998 is apparent followed by a sharp drop in 1999. This drop may be due to the agreement between EPA and the manufacturers to begin phasing out certain uses of chlorpyrifos (see below).

Tables 3-3 and 3-4 show the reported and estimated unreported chlorpyrifos use in Orange County. While overall chlorpyrifos use declined in 1999, nursery use increased by 300 percent. The significant increase in chlorpyrifos use by nurseries is likely due to the requirements imposed by the CDFA under the RIFA program. Runoff of the solution from the treatment area is not permitted (CDFA, March 1999).

Table 3-3: Reported and Estimated Unreported Chlorpyrifos Use
Orange County: 1995-1999 (lbs ai)

Use	1995	1996	1997	1998	1999
Structural	38,263	72,174	69,865	88,985	74,904
Nursery	652	772	971	994	2,913
Agriculture	1,414	952	1,450	645	1,132
Landscape	1,446	1,230	1,374	1,082	1,005
Other non-residential	7	268.5	1.6	1.6	35.3
Reported subtotal	41,782	75,396	73,662	91,707	79,990
Estimated Unreported Residential Use	21,663	40,185	38,859	49,128	41,424
Total	63,445	115,580	112,520	140,835	121,414

ai = active ingredient

Unreported (residential) chlorpyrifos use can be estimated by determining the national ratio of unreported home use to licensed (non-agricultural) use as reported in the USEPA Market Estimates Report (USEPA November 1999). Nationally, in 1995/96, the residential use was estimated at 2-4 million lbs ai, while the licensed (non-agricultural) use was estimated at 4-7 million lbs ai. Using the midpoints of these ranges, the ratio of residential use to licensed non-agricultural use is 0.545 on a national basis. Applying this ratio to the licensed non-agricultural use in Orange County reported to the CDPR for 1999 (75,944 lbs ai) yields an estimate of 41,424 lbs ai unreported residential use (**Table 3-3**). This indicates that the unreported residential use was roughly 34% of the total use in 1999 (**Table 3-4**). Total chlorpyrifos use in the Newport Bay watershed for 1999 would be approximately 24,300 lbs ai (one-fifth of the Orange County total).

Preliminary data from the Sales and Use Survey (Wilen, forthcoming) indicates that retail sales of chlorpyrifos in the Newport Bay watershed may have declined to as little as 546 lbs ai on an annual basis in 2000. This compares to the estimated residential use of 8,285 lbs ai (one-fifth of the Orange County total) presented in **Table 3-3** for 1999. The decline in chlorpyrifos use appears to be a continuation of the trend shown in **Figure 3-2** toward the end of 1999, and is likely related to the re-registration agreement for chlorpyrifos (see below).

Table 3-4: Reported and Estimated Unreported Chlorpyrifos Use
Orange County: 1995-1999 (percent)

Use	1995	1996	1997	1998	1999
Structural	59.2%	61.9%	61.3%	62.7%	60.6%
Nursery	1.0%	0.7%	0.9%	0.7%	2.4%
Agriculture	2.2%	0.8%	1.3%	0.5%	0.9%
Landscape	2.2%	1.1%	1.2%	0.8%	0.8%
Other non-residential	0.0%	0.2%	0.0%	0.0%	0.0%
Reported subtotal	66%	65%	65%	65%	66%
Estimated Unreported Residential Use	34%	35%	35%	35%	34%
Total	100%	100%	100%	100%	100%

An analysis of chlorpyrifos sales data provided by Dow AgroSciences indicates that treatment for wood protection accounts for 70% of urban use (Giesy et al, October 1998). Typical applications involve subsurface injection of chlorpyrifos at relatively high concentrations. Another 14% of urban use was categorized as home use (indoor pests, pet collars, lawns and gardens, building foundations, and other structural applications), while non-residential turf applications accounted for 7% of urban use.

USEPA Phaseout of Certain Chlorpyrifos Uses: In June 2000, the EPA published its revised risk assessment and agreement with registrants for chlorpyrifos (USEPA, June 2000). The agreement imposes new restrictions on chlorpyrifos use in agriculture, cancels or phases out nearly all indoor and outdoor residential uses, and also cancels non-residential uses where children may be exposed. Application rates for non-residential areas where children will not be exposed (golf courses, road medians, industrial plant sites) will be reduced. Public health use for fire ant eradication and mosquito control will be restricted to professionals. Non-structural wood treatments will continue at current rates. Since the EPA estimates that about 50% of the chlorpyrifos use (both licensed and unreported) takes place at residential sites, the agreement is likely to result in at least a 50% decrease in chlorpyrifos use.

In Orange County, residential use (reported and unreported) likely accounts for over 90% of total chlorpyrifos use (most of the reported use is for structural protection applied in and around homes). Thus, it appears that over 90% of the current chlorpyrifos use in the Newport Bay watershed will be eliminated by the EPA agreement. Retail sales are scheduled to stop by December 31, 2001, and structural uses will be phased out by December 31, 2005.

As noted above, the CDPR data, and the preliminary Sales and Use Survey data indicate that chlorpyrifos use has been declining sharply within the last two years. This is likely due to the warning from EPA that retailers should not purchase stock unless they were able to sell it by December 31, 2001. A survey conducted in northern California in late 2000 noted, “Chlorpyrifos products have become increasingly difficult to find” (TDC Environmental, May 2001). It should be noted that the available water-quality data for the Newport Bay watershed, is largely from 1996-2000, and not directly correlated to the latest usage data from 2000-2001.

3.3 ENVIRONMENTAL FATE

The environmental fate of chlorpyrifos and diazinon can be inferred from their physical properties. **Table 3-5** presents properties for diazinon and chlorpyrifos along with several other pesticides that occasionally contribute to the aquatic life toxicity in San Diego Creek. In general, diazinon and chlorpyrifos are a more significant water quality threat because of the combined properties of higher toxicity, mobility, and persistence. Carbaryl for example, is mobile but less toxic and less persistent than diazinon and chlorpyrifos.

Table 3-5: Pesticide Properties

Pesticide	Ceriodaphnia LC50 (ng/L)	Solubility (mg/L)	Adsorption Coefficient	Soil Half-Life	Water Half-Life
Bifenthrin	78	0.1	1,000,000	7 days to 8 months	n/a
Carbaryl	3,380	40	300	7-28 days	10 days
Chlorpyrifos	60	2	6070	2-4 months	1-2.5 months
Diazinon	440	40	1000	2-4 weeks	6 months
DDT	4,700	<1	100,000	2-15 years	1-2 months
Malathion	1,140	130	2.75	1-25 days	< 1 week

source: EXTOXNET Pesticide Information Profiles; CDFG(2000)
n/a=not available

Relative to most pesticides, diazinon is fairly soluble and mobile in aquatic systems. It is only weakly bound by sediment. In contrast, chlorpyrifos is much less soluble and has a much higher potential to adsorb to soil and sediment.

In general, diazinon is relatively persistent in aquatic environments with a half-life of about six-months under neutral pH conditions. The pH of the channel network in the Newport Bay watershed is generally between 7.5 and 8, a range that would maintain the stability of diazinon. In soil, the diazinon half life is shorter owing to greater microbial degradation.

For diazinon, the major routes for dissipation appear to be biodegradation , volatilization, and photolysis (USEPA, May 1999). Degradation is fastest from bare soil, followed by vegetation, and aquatic environments. Biodegradation from impervious urban areas (walkways, pavement) would be slowest due to the relative absence of microbes. This indicates that diazinon may accumulate in residential areas until rainfall runoff carries it into the drainage channel network. In a residential runoff survey conducted in the Castro Valley Creek watershed, diazinon was found in all samples as long as seven weeks after application.

Diazinon dissipation half-lives did not appear to be correlated with formulation type (granular, wettable powder, or emulsifiable concentrate).

The reported diazinon formulations in Orange County for 1999 are listed in **Table 3-6**. The liquid formulations are likely to be the most mobile as they are already in soluble form. The granules would likely remain available until a storm event washed the remaining active ingredient into the storm drains.

Table 3-6: Diazinon Formulations for Reported Uses in Orange County, 1999

Formulation	Use (lbs ai)	Percent
Emulsifiable Concentrate	14,776	60.4%
Granular/Flake	4,675	19.1%
Wettable Powder	2,720	11.1%
Flowable Concentrate	1,969	8.1%
Liquid Concentrate	275	1.1%
Dust/Powder	36.8	0.2%
Pressurized Liquid/Sprays/Foggers	0.465	0.0%
Solution/Liquid (Ready-To-Use)	0.184	0.0%
Total	24,452	100%

Regardless of the formulation used, runoff is likely to occur only after significant rainfall or irrigation. Aside from runoff, a potentially significant discharge could occur through improper disposal of old or leftover material. The degree of knowledge concerning proper disposal varies considerably and it is unlikely that homeowners are able to purchase the exact amount needed.

Large-scale aerial spray applications may drift and result in significant offsite migration. These are generally applied to orchard crops in the Central Valley and, as **Table 3-6** shows, they are not a significant application in Orange County.

There is evidence that the amount of diazinon that reaches the drainage channel network is generally less than one percent of that applied (Scanlin and Feng, 1997). Thus, relatively limited instances of improper use (e.g. inappropriate disposal, excess outdoor application) could account for a large portion of the observed concentrations in the drainage channels.

Compared to diazinon, chlorpyrifos has a shorter half-life in water, but a longer half-life in soil. This is due in part to its higher adsorption coefficient, which results in chlorpyrifos partitioning out of the aquatic phase as it is bound by sediment and soil.

Table 3-7 shows the chlorpyrifos formulations used in Orange County in 1999. As with diazinon, concentrates, powders, and granular/flake formulations account for over 99% of the uses. These formulations require mixing/preparation prior to use.

Table 3-7: Chlorpyrifos Formulations used in Orange County, 1999

Formulation	Use (lbs ai)	Percent
Emulsifiable Concentrate	70,067	87.6%
Wettable Powder	6,571	8.2%
Liquid Concentrate	2,281	2.9%
Granular/Flake	996	1.2%
Pressurized Liquid/Sprays/Foggers	38.1	0.0%
Paint/Coatings	35.1	0.0%
Suspension	1.58	0.0%
Solution/Liquid (Ready-To-Use)	0.103	0.0%
Total	79,990	100%

Of the top four formulations used in Orange County, only the granular/flake formulation would act to slowly release the active ingredient into the water, while the other formulations would enhance mobility. The lower release rate would result in lower concentrations over time.

Dissipation of chlorpyrifos from water takes place through sorption, volatilization, and photolysis. Chemical breakdown (hydrolysis) rates increase with increasing temperature and pH. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis, and biodegradation.

3.4 SOURCES OF DIAZINON AND CHLORPYRIFOS

This section presents an analysis of the sources of diazinon and chlorpyrifos in the Newport Bay Watershed. A summary of the diazinon data is presented in Section 3.5.1, followed by a discussion of diazinon sources categorized by land use in Section 3.5.2. The chlorpyrifos data is summarized in Section 3.5.3, and chlorpyrifos sources categorized by land use are discussed in Section 3.5.4. Point sources (wastewater dischargers) are discussed in Section 3.5.5. Secondary non-point sources, (sediment remobilization, groundwater, and atmospheric deposition) are discussed separately in Sections 3.5.6, 3.5.7, and 3.5.8.

3.4.1 Diazinon Data Summary

Table 3-8 summarizes the results of diazinon sampling in the Newport Bay watershed. The sampling programs are described in **Section 2**. The table shows the high diazinon detection frequency, particularly during stormflow. The observed diazinon concentrations are similar to those observed in urban watersheds elsewhere in California. The median values for both baseflow and stormflow exceed the reference Criterion Chronic Concentration (CCC) and the Criterion Maximum Concentration (CMC). Approximately 98% of the diazinon results collected within the drainage channels exceeded the CDFG CCC of 50 ng/L.

Table 3-8: Summary of Diazinon Sampling Results

Source	Count	No. of Detects	Detection Frequency	Results			
				Min	Max	Average	Median
Water (ng/L)							
Drainage Channels	198	185	93%	<40	10,000	471	220
Baseflow	104	93	89%	<40	10,000	473	160
Stormflow	94	92	98%	<50	7,990	451	357
Upper Newport Bay	26	26	100%	197	720	386	357
Rainfall	1	1	100%	13	13	13	13
Sediment (ug/kg)							
Drainage Channels	98	2	2%	<10	49	---	---
Newport Bay	64	2	3%	<0.4	60	---	---

Numeric Target (ng/L)

Freshwater	CDFG
CCC	50
CMC	80

Source: CDFG, 2000a

For comparison, the median diazinon concentration in the Santa Ana River downstream of Prado dam was 100 ng/L (USGS, 2000), and the detection frequency was 99% (72 of 73 samples). The USGS also reported stormflow concentrations as significantly elevated relative to baseflow concentrations.

The low detection frequency for the sediment samples is in accordance with the moderately low diazinon adsorption coefficient, and its relatively high solubility. All the sediment detections were reported from samples collected in 1994, and diazinon has not been detected in subsequent semi-annual sediment sampling.

Table 3-9: Diazinon Results by Waterbody Group

Waterbody Group	Count	Results (ng/L)				Percent Exceeding	
		Min	Max	Avg.	Median	CCC	CMC
Trib. SDC-R2	24	40	7,990	817	256	96%	92%
Trib. SDC-R1	21	49	628	226	134	86%	67%
Trib.-PCC	41	40	10,000	791	271	83%	78%
PCC	15	170	820	390	367	100%	100%
SDC - R1	59	50	960	301	215	95%	92%
Trib. UNB	35	40	2,250	357	202	94%	91%

Trib. = Tributary; SDC= San Diego Creek; PCC=Peters Canyon Channel
R1, R2 = Reach 1, Reach 2; UNB=Upper Newport Bay

Table 3-9 presents the data summarized by waterbody group. Highest concentrations occur in the upstream tributary channels to San Diego Creek. The maximum concentrations in Hines Channel (which drains into Peters Canyon Channel) were three baseflow samples collected in 1998 with concentrations ranging from 2,500 ng/L to 10,000 ng/L.

The maximum concentration of six baseflow samples collected in Hines channel during 2000, was 323 ng/L, indicating a decrease in usage, or more effective runoff control.

The similarity in median concentrations indicates that there are no clearly dominant areas of the watershed with regard to diazinon loading to San Diego Creek and Upper Newport Bay. Concentrations in Peters Canyon Channel are somewhat elevated relative to the other segments of the drainage network. This was also a conclusion of the 319h study (Lee and Taylor, 2001)

<u>San Diego Creek Reach 2</u>: There were no sampling stations within Reach 2 of San Diego Creek. However, 24 samples were collected from tributary channels (Bee Canyon and Marshburn Slough). These samples were collected several miles upstream of where these channels joined San Diego Creek and were mainly targeted at monitoring nursery discharges. The median concentration for these samples was 256 ng/L, with maximum concentrations of 7,990 ng/L during stormflow and 2,320 ng/L during baseflow. Over 95% of the samples collected exceeded the CCC, while 92% exceeded the CMC.

<u>San Diego Creek Reach 1</u>: The main tributary to San Diego Creek Reach 1, (aside from Reach 2), is Peters Canyon Channel. Median diazinon concentrations in Peters Canyon Channel (367 ng/L) were higher than in San Diego Creek (208 ng/L). The median concentration for other tributaries to San Diego Creek was 143 ng/L. All 15 samples collected within PCC exceeded both the CCC and CMC, while in the tributary channels to the PCC, the percentages exceeding the CCC and CMC were lower, 83% and 78% respectively. For samples collected within Reach 1 itself, 95% exceeded the CCC and 92% exceeded the CMC.

<u>Upper Newport Bay</u>: The median concentration for drainage channels discharging directly to Upper Newport Bay (East Costa Mesa, Westcliff Park, Santa Ana Delhi) was 202 ng/L. The CDFG has not recommended a CCC or CMC for diazinon in saltwater, however, the LC-50 for the commonly used test species (*Mysidopsis bahia*) is 4,200 ng/L, and the observed diazinon concentrations were all below this level, with a maximum of 720 ng/L. The USEPA (USEPA, August 2000b) has published draft recommended acute and chronic criteria for diazion in saltwater (820 ng/L and 400 ng/L respectively). The maximum and average results from Upper Newport Bay were below the respective draft USEPA saltwater CMC and CCC.

3.4.2 Diazinon Sources Categorized by Land Use

Tables 3-10a and 3-10b present the diazinon results by sampling location along with the land use pattern in the monitored sub-watershed. The locations in **Table 3-10a** are sorted according to median stormwater runoff concentration, while in **Table 3-10b**, they are sorted according to median baseflow concentration. Several of the locations were sampled for only baseflow or only stormflow conditions.

Table 3-10a: Land Use and Diazinon Stormflow Concentrations
Newport Bay Watershed: 1996-2000

			Stormflow Results (ng/L)			
Station	Land Use	Count	Min	Max	Avg.	Median
Westcliff Park	residential	7	174	1,079	692	678
Drain at Bee Canyon and Portola Pkwy.	nursery	7	126	7,990	1,625	599
Central Irvine Channel – Monroe	ag (nursery)-residential	2	90	810	545	545
Peters Canyon Channel – Walnut	mixed	1	520	520	520	520
East Costa Mesa Channel - Highland Dr.	residential	2	370	560	465	465
Bonita Creek at San Diego Creek	residential	7	69	628	424	456
San Diego Creek - Campus Dr.	mixed	25	96	960	445	375
El Modena-Irvine Channel upstream of PCC	residential	1	330	330	330	330
Hines Channel - Irvine Blvd.	nursery	9	199	810	455	324
Peters Canyon Channel – Barranca	mixed	10	202	426	321	309
San Diego Creek - Harvard Av.	mixed	2	200	280	240	240
Santa Ana Delhi Channel – Mesa Dr.	residential-urban	10	64	375	171	174
Marshburn Slough - Irvine Blvd.	Nursery	7	96	291	168	136
Sand Canyon Ave - NE corner Irvine Blvd.	agricultural	2	70	110	90	90
San Joaquin Creek - Univ Dr.	agricultural-open	2	<50	<50	<50	<50

At virtually all the locations, the median stormflow concentration is significantly higher than the median baseflow concentration. Since stormwater runoff constitutes about 80% of the volume of water discharged to Newport Bay on an annual basis, this would indicate that the overwhelming majority of the pesticide load would derive from stormflow rather than baseflow. The average concentration is actually higher for baseflow, but this is biased by a few very high detections from 1998 near nurseries. These results have not been observed in later sampling and the nurseries have subsequently instituted measures targeted at reducing pesticide runoff.

Although the sampling network is not detailed enough to identify individual sources (aside from nurseries), two conclusions are apparent:

(1) Stormflow concentrations are virtually always higher than baseflow concentrations. This is particularly the case in the non-agricultural areas.
(2) Residential areas tend to yield the highest stormwater runoff concentrations while the nursery areas tend to yield the higher baseflow concentrations.

These conclusions were also evident in the 319h study (Lee and Taylor, 2001). The 319h study monitored pesticide concentrations in runoff and correlated this with land use in the sub-watershed.

Studies reported in the literature indicate that residential hotspots (individual homes) can account for most of the diazinon runoff from a neighborhood. Samples collected from the near vicinity of these residential hotspots (prior to dilution in the storm drain), showed concentrations above 10,000 ng/L (Scanlin and Feng, 1997). Such detailed sampling and analysis for pesticides has not been conducted in residential areas of the Newport Bay watershed.

Table 3-10b: Land Use and Diazinon Baseflow Concentrations
Newport Bay Watershed: 1996-2000

Station	Land Use	Count	Baseflow Results (ng/L)			
			Min	Max	Avg.	Median
Hines Channel - Irvine Blvd.	nursery	10	47	10,000	2,129	862
Drain at Bee Canyon and Portola Pkwy.	nursery	7	93	2,320	977	637
Central Irvine Channel – Bryan St	agricultural-residential	5	117	1,940	722	570
Peters Canyon Channel - Barranca	mixed	4	170	820	533	570
Central Irvine Channel - Monroe	ag (nursery)-residential	2	90	840	465	465
San Diego Creek - Coronado St.	mixed	2	94	365	230	230
Westcliff Park	residential	9	<40	2,250	432	215
East Costa Mesa Channel - Highland Dr.	residential	1	210	210	210	210
El Modena-Irvine Channel upstream of PCC	residential	1	180	180	180	180
San Diego Creek - Campus Dr.	mixed	28	<50	570	200	160
Santa Ana Delhi Channel - Mesa Dr.	residential-urban	6	<50	340	149	125
Bonita Creek at San Diego Creek	residential	12	49	332	139	114
El Modena	nursery	3	<40	310	146	87
San Diego Creek - Harvard Av.	mixed	2	<50	<50	<50	<50
Marshburn Slough - Irvine Blvd.	nursery	1	<40	<40	<40	<40
Hines at Weir	nursery	5	<40	45	41	<40

3.4.3 Chlorpyrifos Data Summary

Table 3-11 summarizes the chlorpyrifos results. The detection frequency is lower than for diazinon. This is due in part, to the lower solubility of chlorpyrifos, and its greater affinity for sediment (**Table 3-5**). As discussed in **Section 3-4**, the lower mobility of chlorpyrifos results in lower concentrations in the drainage channels, despite the fact that over twice as much chlorpyrifos is applied as compared to diazinon (lbs ai) (**Tables 3-1 and 3-3**),

The average values for stormflow and baseflow exceed the numeric target Criterion Chronic Concentration (CCC). Within the drainage channels, 44% of the chlorpyrifos results exceeded the CCC of 14 ng/L, while 92% of the samples collected in Upper Newport Bay were above the saltwater CCC of 9 ng/L.

Table 3-11: Summary of Chlorpyrifos Sampling Results

Source	Count	No. of Detects	Detection Frequency	Results			
				Min	Max	Average	Median
Water (ng/L)							
Drainage Channels	198	89	45%	ND	770	139	<50
Baseflow	104	36	35%	ND	670	162	<40
Stormflow	94	53	56%	ND	770	123	50
Upper Newport Bay	24	24	100%	2	132	43.3	41.5
Rainfall	1	1	100%	23	23	23	23
Sediment (ug/kg)							
Drainage Channels	2	2	100%	17	29	23	23

Numeric Targets (ng/L)

Freshwater	
CCC	14
CMC	20
Saltwater	
CCC	9
CMC	20

Source: CDFG, 2000a

The sediment data for chlorpyrifos is reflective of the higher soil adsorption coefficient relative to diazinon. Although chlorpyrifos analyses were not presented in the OCPFRD data, chlorpyrifos was detected in both sediment samples collected by the CDFG.

Table 3-12: Chlorpyrifos Results by Waterbody Group

Waterbody Group	Count	Results (ng/L) Max	Avg.	Median	Detection Frequency
Trib-SDC-R2	24	121	51	<40	33%
Trib-SDC-R1	21	770	95	<40	10%
Trib-PCC	41	670	108	50	54%
PCC	15	420	83	57	60%
SDC-R1	59	580	102	57	59%
Trib-UNB	35	231	47	<40	37%
UNB	24	132	43.3	41.5	100%

Trib. = Tributary; SDC= San Diego Creek; PCC=Peters Canyon Channel; R1, R2 = Reach 1, Reach 2; UNB=Upper Newport Bay

Table 3-12 presents the data summarized by waterbody group. Detection frequencies were low, particularly in the upper reaches of the watershed. Detection frequencies were higher in Peters Canyon Channel and its tributaries, where a large proportion of the samples were from undiluted nursery discharges. Comparison to the CCC and CMC is difficult because they are set at levels below the analytical reporting limit used for most of the sampling programs.

<u>San Diego Creek Reach 2</u>: There were no samples collected from within Reach 2, however, samples collected from tributary channels discharging into Reach 2 had a low detection frequency (33%) and a maximum concentration of 121 ng/L.

<u>San Diego Creek Reach 1</u>: Samples collected from locations in Reach 1 of San Diego Creek (at Campus, Coronado, and Harvard streets) had a relatively high detection frequency and the highest median concentration, along with Peters Canyon Channel. This may indicate that the greater part of the chlorpyrifos loading is derived from Peters Canyon Channel and its sampled tributaries (Hines, Central Irvine). However, the maximum chlorpyrifos concentrations occurred in two samples collected from San Joaquin Creek, which discharges directly into Reach 1 of San Diego Creek.

<u>Upper Newport Bay</u>: Chlorpyrifos was detected in all samples collected in Upper Newport Bay, where a lower detection limit was employed. The samples were collected over several days during a storm event in January 1999. The chlorpyrifos concentration that saltwater organisms are exposed to is largely dependent on the degree of mixing between saltwater and freshwater in the upper bay. In the case of the storm sampled in January 1999, a freshwater lens persisted for several days in the upper bay. Chlorpyrifos concentrations were inversely correlated with salinity. Overall, the observed concentrations were lower in Upper Newport Bay than in San Diego Creek.

3.4.4 Chlorpyrifos Sources Categorized by Land Use

Tables 3-13a and 3-13b present the chlorpyrifos results by sampling location along with the land use pattern in the monitored sub-watershed. The locations in **Table 3-13a** are sorted according to median stormwater runoff concentration, while in **Table 3-13b**, they are sorted according to median baseflow concentration.

Stations sampling runoff derived from mixed land use areas tended to have the highest chlorpyrifos concentrations under both baseflow and stormflow conditions. A major exception was the data from San Joaquin Creek. This creek was sampled during two separate storm events in February, 2000. (Baseflow samples were not collected). The results were the two highest chlorpyrifos concentrations (770 ng/L and 470 ng/L) in the entire dataset.

This sample was also associated with very high concentrations of carbaryl that were determined to originate from agricultural fields planted with strawberries that were treated with pesticides immediately prior to a rainfall event.

Chlorpyrifos was not detected in the two stormflow samples collected at the second non-nursery agricultural location (Sand Canyon Ave - NE corner Irvine Blvd). Therefore, assigning a median concentration to the entire watershed for non-nursery agriculture based on this limited data may be unwarranted.

It is difficult to draw strong conclusions from the data in **Tables 3-13a and 3-13b** due to the limited number of samples at most of the locations, and the large number of non-detect results. The chlorpyrifos results also do not correlate well with the diazinon results; the locations with the higher diazinon concentrations do not generally yield the higher chlorpyrifos concentrations. The sampling locations at Westcliff Park and the Central Irvine Channel at Monroe were the only locations among the top seven stormflow results for both chlorpyrifos and diazinon. The baseflow results had a somewhat better correlation, but overall the data suggest differing usage patterns for chlorpyrifos and diazinon.

Sample locations monitoring residential areas tended to have lower chlorpyrifos concentrations. Chlorpyrifos was not detected at three of the residential locations under either baseflow or stormflow conditions. The detection frequency, and maximum concentrations detected at another partly residential location (Santa Ana Delhi Channel) were low. The only residential site with relatively high chlorpyrifos concentrations was Westcliff Park (stormflow), but the baseflow concentrations were relatively low.

Although it appears that some of the nursery/agricultural locations yield higher chlorpyrifos concentrations than the residential areas, it should be noted that the nursery monitoring locations are selected to monitor undiluted nursery discharge, very close to where the chlorpyrifos is used. In contrast, runoff from individual homes where chlorpyrifos is applied is not monitored, since the monitoring location is within a channel collecting mixed/diluted runoff from many homes. In addition, because of the relative immobility of chlorpyrifos, and its tendency to adsorb to sediment, higher chlorpyrifos concentrations are most likely to be encountered only near areas where it is applied, before it partitions out of the aqueous phase and settles out along with the sediment.

Table 3-13a: Land Use and Stormflow Chlorpyrifos Concentrations
Newport Bay Watershed: 1996-2000

Station	Land Use	Count	Results (ng/L)			
			Min	Max	Avg	Median
San Joaquin Creek - Univ Dr.	agricultural-open	2	470	770	620	620
San Diego Creek - Harvard Av.	mixed	2	190	310	250	250
Central Irvine Channel - Monroe	ag(nursery)-residential	2	70	150	110	110
Westcliff Park	residential	9	<40	231	97	94
Peters Canyon Channel - Barranca	mixed	10	<40	102	72	69
Marshburn Slough – Irvine Blvd.	nursery	7	45	121	74	62
San Diego Creek - Campus Dr.	mixed	25	<40	260	87	57
Hines Channel - Irvine Blvd.	nursery	9	<40	349	98	<50
Santa Ana Delhi Channel - Mesa Dr.	residential-urban	10	<40	55	48	<40
Drain at Bee Canyon and Portola Pkwy.	nursery	7	<40	60	43	<40
Sand Canyon Ave - NE corner Irvine Blvd.	agricultural	2	<50	<50	<50	<50
East Costa Mesa Channel - Highland Dr.	residential	2	<50	<50	<50	<50
El Modena-Irvine Channel upstream of PCC	residential	1	<50	<50	<50	<50
Bonita Creek at San Diego Creek	residential	7	<40	<40	<40	<40

Table 3-13b: Land Use and Baseflow Chlorpyrifos Concentrations
Newport Bay Watershed: 1996-2000

Station	Land Use	Count	Results (ng/L)			
			Min	Max	Avg	Median
San Diego Creek – Harvard Av.	mixed	2	50	400	225	225
Central Irvine Channel – Monroe	ag(nursery)-residential	2	<50	281	166	166
Peters Canyon Channel - Walnut	mixed	1	150	150	150	150
Central Irvine Channel - Bryan St	agricultural-residential	5	<40	315	164	117
Hines Channel - Irvine Blvd.	nursery	10	40	670	158	88
San Diego Creek – Campus Dr.	mixed	28	<40	580	111	56
Peters Canyon Channel - Barranca	mixed	4	50	420	144	54
El Modena	nursery	3	<40	57	49	49
Santa Ana Delhi Channel - Mesa Dr.	residential-urban	6	<40	50	37	<40
East Costa Mesa Channel - Highland Dr.	residential	1	<50	<50	<50	<50
El Modena-Irvine Channel upstream of PCC	residential	1	<50	<50	<50	<50
Westcliff Park	residential	7	<40	129	51	<40
Marshburn Slough - Irvine Blvd.	nursery	1	<40	<40	<40	<40
Hines at Weir	nursery	5	<40	63	45	<40
Drain at Bee Canyon and Portola Pkwy.	nursery	7	<40	<40	<40	<40
San Diego Creek - Coronado St.	mixed	2	<40	<40	<40	<40
Bonita Creek at San Diego Creek	residential	12	<40	<40	<40	<40

3.4.5 Point Sources (Wastewater Dischargers)

There are over fifteen waste discharge requirement (WDR) and NPDES permit holders in the Newport Bay watershed. Some of these permits are in the process of being rescinded.

NPDES
Five of the NPDES permits are minor permits for discharge of extracted groundwater. These are not expected to be sources of diazinon and chlorpyrifos loads to the watershed (groundwater is discussed further below), and the dischargers are not required to monitor for OP pesticides. The other two NPDES permits are classified as major permits and are discussed below.

NPDES - Stormwater Runoff:
Stormwater runoff in the Newport Bay watershed is regulated by an NPDES permit for Orange County. As discussed in Section 2, the OCPFRD monitoring program does not include analysis for organophosphate pesticides. However, considerable data have been collected from stormwater runoff channels as part of the 205j, 319h, and CDPR investigations.

NPDES - Sewage Treatment Plants:
Diazinon has been found in effluent from STPs (USEPA, May 1999). Presumably, the diazinon results from improper disposal of surplus pesticides into sewer drains. The Newport Bay Watershed residential use survey has indicated a lack of knowledge among homeowners concerning proper disposal procedures (Wilen, forthcoming). The only STP in the Newport Bay Watershed (IRWD STP), does not discharge effluent to the drainage channels or Newport Bay.

WDR
Nursery WDRs:
There are three commercial nurseries in the Newport Bay watershed that are regulated under WDRs. WDRs are being prepared for an additional two nurseries. Together, these nurseries account for less than two percent of the area in the Newport Bay Watershed. As part of the nutrient TMDL for Newport Bay (1999) nurseries greater than five acres and discharging to tributaries that enter Newport Bay were required to institute a regular monitoring program. The monitoring program includes bi-monthly monitoring for toxicity, however, there is no requirement for analysis of OP pesticides. Several of the sampling locations for the 205j, 319h and DPR-RIFA studies were chosen to monitor discharges from nurseries to the drainage channel network. The highest diazinon results occurred in Hines channel and the Drain at Bee Canyon and Portola Parkway sampling station. These results reflect relatively undiluted discharge from agricultural (mostly nursery) areas.

Other WDRs:
Several other facilities (including three landfills) have WDRs but none are required to monitor for OP pesticides, and they are not considered to be significant sources of OP pesticide loads.

3.4.6 Groundwater

Although there are no currently available groundwater data for diazinon and chlorpyrifos in the Newport Bay watershed, groundwater does not appear to be contributing diazinon and chlorpyrifos loads to the drainage system. Diazinon and chlorpyrifos concentrations are lower downstream of areas where groundwater seeps into the drainage channels. This indicates that the groundwater serves to dilute the concentrations.

In general, diazinon and chlorpyrifos tend to dissipate from the ground surface or in the upper soil layers before percolating to groundwater. Diazinon and chlorpyrifos have not been detected in groundwater sampling conducted by the USGS in the lower Santa Ana River Basin.

3.4.7 Sediment Remobilization

As discussed in the fate and transport section, diazinon has a relatively low potential to adsorb to sediment while chlorpyrifos has a greater adsorption coefficient (**Table 3-5**). Chlorpyrifos could accumulate in sediment and be gradually released into the water through desorption. This would require stability of the adsorbed chlorpyrifos, but adsorbed chlorpyrifos is still subject to chemical hydrolysis and biodegradation.

The available sediment data demonstrate that diazinon is not being bound to sediment. As shown in **Table 3-8**, the detection frequency for diazinon in sediment samples is less than two percent.

Two sediment samples were collected by the CDFG in July/August 2000. Chlorpyrifos was detected in sediment from Hines channel (29 ng/g) and in sediment collected nine miles downstream from the nurseries in San Diego Creek (17 ng/g) (CDFG, October 2000). Diazinon was not detected at either location (reporting limit of 10 ng/g dry weight)

As part of the semi-annual sampling program, the OCPFRD collected 96 sediment samples from the Newport Bay watershed and 54 sediment samples from the Bay itself from 1994-1999. Only four diazinon detections were reported. All the detections occurred in 1994, at concentrations of 40 ug/kg to 60 ug/kg. Reporting limits ranged from 35 ug/kg to 400 ug/kg. OCPFRD does not currently monitor sediment for chlorpyrifos.

3.4.8 Atmospheric Deposition

Diazinon is one of the most frequently detected pesticides in air, rain, and fog (USEPA, May 1999). In sampling conducted in California in 1988, diazinon was detected in approximately 90% of the sites sampled. Chlorpyrifos has a vapor pressure in the same range as diazinon, and can be expected to volatilize from treated areas. It is not as commonly detected in the atmosphere however.

A rainwater sample collected in the Newport Bay watershed during the 205j studies (December 1997) was reported to have a diazinon concentration of 13 ng/L and a chlorpyrifos concentration of 23 ng/L (Lee and Taylor, 1999).

For comparison, eight rainwater samples collected in the Castro Valley Creek watershed, an urban watershed in northern California, had a mean diazinon detected concentration of 58 ng/L with a maximum of concentration of 88 ng/L (Katznelson and Mumley, 1997).

Higher diazinon concentrations in rainwater have been detected in agricultural areas (over 5,000 ng/L in 1994-95, and ranging from 418 ng/L to 5,463 ng/L in 14 cities located in the Central Valley) but these are likely related to aerial spray applications to orchards – a type of use that is negligible in the Newport Bay Watershed. Rainfall collected in the winter of 1992-93 in the San Joaquin basin contained up to 1,900 ng/L diazinon. The source of this diazinon is “presumed to be droplets from dormant spray applications (not volatilization from treated crops)” (Novartis, 1997).

<u>Indirect deposition</u>: Assuming the measured rainfall concentration is representative for all storm events, and assuming no degradation during runoff, the annual diazinon load derived from rainfall would be approximately 0.72 lbs. This would be about 3.4% of the total annual load to Newport Bay. For chlorpyrifos, the load would be 1.27 lbs, which would be about 33% of the total annual load to Newport Bay. It is uncertain however whether this contribution is from volatilization from use within the watershed, or is from aerial transport from outside the watershed. If the origin is from within the watershed, then the contribution from rainfall is already taken into account by the runoff sampling. Origin from outside the watershed would be a significant source for chlorpyrifos. Further study of aerial transport and deposition of pesticides is required. A forthcoming study funded by the DPR will address this issue in the Southern California region.

<u>Direct deposition</u>: Direct deposition (rainfall falling directly onto Newport Bay) would be negligible since the area of the bay relative to the watershed is less than one percent. The diazinon load would be less than 0.0072 lbs, or less than 0.03% of the annual load to the Bay. For chlorpyrifos the load would be 0.0127 lbs or about 0.3% of the total annual load.

3.5 CURRENT LOADING

This section presents calculations of diazinon and chlorpyrifos loads to San Diego Creek and Upper Newport Bay.

3.5.1 Diazinon

The calculated runoff loading based on flow and concentration data from the Newport Bay watershed is about 32 lbs annually (**Table 3-14**). This amounts to 0.24% of the estimated 10,700 lbs of diazinon (ai) that was used within the watershed in 1999. This finding is similar to the result reported in a recent study in the Castro Valley watershed (an urban watershed). The study found that 0.3% of the applied diazinon (ai) was discharged into Castro Valley Creek and that 90% of this load was delivered by stormwater runoff (Scanlin and Feng, 1997).

Table 3-14: Diazinon Current Loads

Waterbody	Annual Flow (acre-ft)	Median Conc. (ng/L)	Load (lbs)	Load (percent)
S. D. Creek Reach 2				
Baseflow	4,374	160	2.5	14%
Stormflow	16,919	375	15.9	86%
		Total:	**18.4**	100%
S. D. Creek Reach 1				
Baseflow	7,674	160	4.4	14%
Stormflow	29,682	375	27.8	86%
		Total:	**32.2**	100%

Note: Samples have not been collected from Reach 2 of San Diego Creek. For the purposes of calculating current loads, the median concentration for Reach 2 of San Diego Creek is set equal to the median concentration for Reach 1.

Table 3-15 presents summary diazinon results categorized by land use, and estimates of the annual load for baseflow and stormflow. Only samples from locations where either urban or non-urban (agriculture, nursery) land use predominated were included in generating the table; about 40% of the samples in the data set were excluded.

Table 3-15: Diazinon Concentrations and Loads by Land Use

Condition	LandUse	Count	Results (ng/L) Min	Max	Avg	Median	Area (acres)	Area (%)	Load (lbs)	Load (%)	Load (lbs/acre)
Baseflow	urban	27	<40	2,250	236	140	66,507	68%	2.4	88.4%	3.61E-05
	agriculture	27	<40	10,000	1,002	131	9,286	10%	0.31	11.6%	3.38E-05
	open	---	---	---	---	---	21,948	22%	0.0	0.0%	0.00E+00
	Total						97,741	100%	**2.7**	100%	2.78E-05
Stormflow	urban	27	64	1,079	400	370	66,507	68%	24.1	96.3%	3.63E-04
	agriculture	27	<50	7,990	627	271	9,286	10%	2.47	2.1%	2.66E-04
	open	---	---	---	---	---	21,948	22%	0.0	0.0%	0.00E+00
	Total						97,741	100%	**26.6**	100%	2.72E-04

Land use data: Jan, 2000 Orange County Planning and Development Services Department, in (in Newport Bay/San Diego Creek Watershed Study; Feb 2001)

The total diazinon load estimated from **Table 3-15** is not directly comparable with the total load calculated using the average data from San Diego Creek (**Table 3-14**) because the data sets are different. The table is simply intended to compare export rates from urban and agricultural areas. On a per-acre basis, diazinon export rates appear to be slightly higher for urban areas than for agricultural areas.

The intensive residential investigation in the Castro Valley Creek watershed (Scanlin and Feng, 1997) revealed that a small number of individual residential hotspots (2% to 4% of the homes) produced the bulk of the diazinon loading to the Creek. Controlled experiments to evaluate diazinon runoff from individual homes demonstrated that even when diazinon was used properly, and the label directions scrupulously followed, very high levels of diazinon would still be produced in the runoff. Highest source areas were patios and driveways, followed by roof drains. These results are probably due to the lower rates of dissipation from these surfaces as compared to lawns or soil, where biodegradation would be much more significant.

3.5.2 Chlorpyrifos

Table 3-16 presents an estimate of the annual chlorpyrifos loading to San Diego Creek and Upper Newport Bay. The total annual mass of chlorpyrifos entering Upper Newport Bay is about 7.3 pounds. This is about 0.03% of the estimated 24,300 lbs ai of chlorpyrifos applied in the watershed (one-fifth of the Orange County total given in **Table 3-3**). This load is based on a conservative estimate of chlorpyrifos concentrations in tributaries to Upper Newport Bay. Actual concentrations in Upper Newport Bay would be reduced due to mixing and dilution.

Table 3-16: Chlorpyrifos Current Loads

Waterbody	Annual Flow (acre-ft)	Median Conc. (ng/L)	Load (lbs)	Load (percent)
S. D. Creek Reach 2				
Baseflow	4,374	56	0.89	24%
Stormflow	16,919	57	2.75	76%
		Total:	**3.6**	100%
S. D. Creek Reach 1				
Baseflow	7,674	56	1.6	24%
Stormflow	29,682	57	4.8	76%
		Total:	**6.4**	100%
Upper Newport Bay				
Baseflow	9,281	53	1.9	24%
Stormflow	35,236	61	5.4	76%
		Total:	**7.3**	100%

Note: Because samples have not been collected from Reach 2 of San Diego Creek, the median concentration for Reach 2 is set equal to the median concentration for Reach 1. The total load entering Upper Newport Bay is estimated by adding flow data and median chlorpyrifos concentrations from the Santa Ana Delhi channel.

Table 3-17 presents chlorpyrifos concentrations and loads categorized by land use for the baseflow and stormflow conditions. Compared to diazinon, urban areas contribute a lesser percentage of the stormflow chlorpyrifos load. On a per-acre basis, export rates for urban and agricultural areas are similar. The total chlorpyrifos load estimated from **Table 3-17** is not directly comparable with the total load calculated using the data from San Diego Creek (**Table 3-16**). The discrepancy between the two methods results from the differing data sets.

Table 3-17: Chlorpyrifos Concentrations and Loads by Land Use

			Results (ng/L)				Area		Load		Load
Condition	LandUse	Count	Min	Max	Det Freq.	Median	(acres)	(%)	(lbs)	(%)	(lbs/acre)
Baseflow	urban	27	nd	129	14%	<40	66,507	68%	0.69	87.7%	1.03E-05
	agriculture	27	<40	670	35%	<40	9,286	10%	0.10	12.3%	1.03E-05
	open	---	---	---	---	---	21,948	22%	0.00	0.0%	0.00E+00
	Total						97,741	100%	**0.78**	100%	8.01E-06
Stormflow	urban	27	nd	231	33%	<40	66,507	68%	2.61	85.1%	3.92E-05
	agriculture	27	<40	770	56%	50	9,286	10%	0.46	14.9%	4.90E-05
	open	---	---	---	---	---	21,948	22%	0.00	0.0%	0.00E+00
	Total						97,741	100%	**3.06**	100%	3.13E-05

3.6 SUMMARY AND CONCLUSIONS

1. Reported and unreported urban uses account for over 90% of total diazinon and chlorpyrifos use in Orange County and in the Newport Bay Watershed.

2. About 32 pounds of diazinon are discharged annually to San Diego Creek, mostly during storm events. This amounts to about 0.24% of the applied diazinon mass in the watershed. About 7 pounds of chlorpyrifos are annually discharged to Upper Newport Bay, with 76% of the load delivered during storm events. This amounts to about 0.03% of the applied chlorpyrifos mass.

3. Surface runoff is the source of virtually all the loadings. Contributions from atmospheric deposition, sediment remobilization, and groundwater are negligible. An exception would be atmospheric transport and deposition of diazinon and chlorpyrifos originating from outside of the Newport Bay watershed. Further investigation would be required to determine whether this is an important source of pesticide loading to San Diego Creek and Newport Bay.

4. On a per acre basis, different land uses contribute diazinon and chlorpyrifos runoff at fairly equal rates within the watershed.

5. Runoff derived from urban land uses accounts for about 88% of the diazinon baseflow load, and 96% of the stormflow load. Agricultural sources (including nurseries) account for the remainder of the load.

6. For chlorpyrifos, runoff derived from urban land uses accounts for about 85% to 88% of the baseflow and stormflow loads, while agriculture (including nurseries) accounts for about 12% to 15% of the load.

7. Average diazinon concentrations in San Diego Creek exceed the chronic numeric target (CCC) of 50 ng/L both during baseflow (200 ng/L) and during stormflow (445 ng/L).

8. Average chlorpyrifos concentrations in San Diego Creek exceed the CDFG CCC (14 ng/L) during baseflow (111 ng/L) and stormflow (87 ng/L). The average chlorpyrifos concentration in Upper Newport Bay (43.3 ng/L) exceeds the saltwater chronic numeric target (CCC) of 9 ng/L.

9. The diazinon re-registration agreement by EPA will likely end over 90% of current diazinon use in the Newport Bay watershed. If runoff concentrations show a corresponding decline, diazinon concentrations in San Diego Creek could decrease below the chronic numeric target (50 ng/L).

10. The chlorpyrifos re-registration agreement by EPA will likely end over 90% of current chlorpyrifos use in the Newport Bay watershed. If runoff concentrations show a corresponding decline, chlorpyrifos concentrations in San Diego Creek and Upper Newport Bay could decline below the respective chronic numeric targets for freshwater and saltwater.

4.0 LOAD ALLOCATION

4.1 INTRODUCTION

TMDLs, while commonly expressed as loads, can also be expressed using other measures. The TMDL regulations state; "TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measure" [40 CFR 130.2(i)].

For the diazinon and chlorpyrifos TMDLs, the concentration is the most appropriate measure. This is because the beneficial use impairment is due to toxic concentration levels in the aquatic environment. The numeric target consists of an acute and chronic criterion averaged on a 1-hour and 4-day time period, respectively. Setting the TMDL based on daily or annual loads could subject aquatic organisms to unacceptable adverse effects. This is because short-term concentrations could exceed the acute or chronic numeric targets while the average concentration indicated by the mass load would suggest compliance with the numeric targets.

The TMDL is therefore expressed using the chronic and acute concentration limits derived by the CDFG for these pesticides for the protection of aquatic life. The TMDL numeric targets apply to Reach 1 and Reach 2 of San Diego Creek (chlorpyrifos and diazinon) and to Upper Newport Bay for chlorpyrifos.

These numeric targets can be expressed as loads (mass per time) by multiplying the concentrations by the flow rates in San Diego Creek. The mass loads can be used to analyze the relative contributions of different dischargers to the total load. However, the concentration criteria will be used to measure compliance with the TMDL, not the mass loads.

4.2 ASSIMILATIVE CAPACITY

The assimilative capacity for diazinon and chlorpyrifos is based on comparison of stormwater samples in San Diego Creek to the chronic numeric target, and comparison of maximum observed concentrations to the acute numeric target. The chronic numeric target identifies the maximum continuous concentration that could be tolerated without adverse impacts. Concentration fluctuations are taken into account through expression of the chronic criterion as a four-day average. The allowed frequency of exceedance is once every three years. This interval is judged sufficient to allow impaired populations to recover (USEPA, 1985).

Because the chronic criterion is a four-day average, available time-series stormwater data from San Diego Creek were averaged and the highest average concentration for diazinon and chlorpyrifos were selected. For diazinon, the highest average concentration in San Diego Creek was from a storm event in January 1999, with samples collected over a three-day period (**Table 4-1**). In the case of chlorpyrifos, the highest stormwater concentration was from a sampling event in February 2000, where only a single sample was available (**Tables 4-2**).

The chronic criterion is paired with an acute criterion, which serves as a maximum concentration. Similar to the chronic criterion, exceedance of this concentration (a one-hour average) is allowed once every three years. To illustrate the needed reduction required for compliance with the acute criterion, the single maximum concentrations in San Diego Creek (baseflow or stormflow) were compared to the respective diazinon and chlorpyrifos acute numeric targets.

Table 4-1: Diazinon Stormwater Sampling in San Diego Creek

Dates	Average (ng/L)	No. Samples
Jan 25-27, 1999	848	4
Jan 25-26, 2000	595	6
12-Feb-00	460	1
Mar 25-26, 1998	301	4
May 12-13, 1998	294	5
21-Feb-00	220	1
06-Dec-97	216	4
24-Feb-00	135	1

Table 4-2: Chlorpyrifos Stormwater Sampling in San Diego Creek

Date	Average (ng/L)	No. Samples
12-Feb-00	260	1
21-Feb-00	170	1
Jan 25-26, 2000	120	6
24-Feb-00	101	1
06-Dec-97	70	4
May 12-13, 1998	59	5
Mar 25-26, 1998	50	4
Jan 25-27, 1999	50	4

Table 4-3 shows the needed load (concentration) reductions for diazinon and chlorpyrifos in order to achieve the TMDL numeric targets in San Diego Creek. The difference between the assimilative capacity and the current load is the required reduction. Chlorpyrifos concentrations may have begun to decline in 2000 and 2001, based on indications of a reduction in usage from the DPR database as well as from the Sales and Use Survey (Wilen, forthcoming) conducted in late 2000. There are as yet no clear indications of declining trends in diazinon usage in the watershed.

Table 4-3: Needed Load (Concentration) Reductions

	San Diego Creek (1996-2001)		TMDL		Needed Reduction	
Constituent	**Storm Average (ng/L)**	**Maximum (ng/L)**	**Chronic (ng/L)**	**Acute (ng/L)**	**Chronic (ng/L)**	**Acute (ng/L)**
Chlorpyrifos	260	580	14	20	95%	97%
Diazinon	848	960	50	80	94%	92%

4.3 MARGIN OF SAFETY

The TMDL regulations (40 CFR 130.7) require that "TMDLs shall be established at levels necessary to attain and maintain the applicable narrative and numerical water quality standards with seasonal variations and a margin of safety which takes into account any lack of knowledge concerning the relationship between effluent limitations and water quality."

As discussed in **Section 2.1** the chronic and acute concentration limits as derived by the CDFG, include a margin of safety. In addition, the following conservative assumptions have been used in developing the load allocation and analyzing the needed reductions.

1. No consideration of pesticide breakdown from point of discharge to San Diego Creek. The half-lives of diazinon and chlorpyrifos in water range from a few days up to six months, but faster biotic or abiotic degradation can occur depending on site-specific conditions.

2. No consideration of mixing and dilution within the drainage channels. In particular, the dilution capacity provided by groundwater seepage into the drainage channel network has not been factored into the TMDL.

3. Calculation of assimilative capacity was performed using arithmetic averages of the data set, with non-detect results set equal to the detection limit. This likely overestimates the current load as the detection frequency for chlorpyrifos in San Diego Creek was less than 60%.

4.4 LOAD and WASTE LOAD ALLOCATIONS

Table 4-4 presents interim and final TMDL allocations for diazinon and chlorpyrifos. The final allocations are based on the numeric target. The interim allocation schedule is intended to provide a reasonable period of adjustment commensurate with the EPA phaseout agreements. The interim allocation for diazinon is based on the draft EPA recommended water quality criteria for diazinon that was published in 2000 (USEPA, August 2000b) and calculated using the USEPA methodology established in 1985 (USEPA 1985). As both the acute and chronic criteria were equal to 100 ng/L in this draft document, the interim allocation for diazinon is expressed as a maximum.

The interim allocation for chlorpyrifos is equal to one-half the *Ceriodaphnia dubia* LC50 (60 ng/L). *Ceriodaphnia dubia* was the most sensitive species in the CDFG data set that used to derive the acute and chronic recommended criteria for chlorpyrifos. The interim allocation for chlorpyrifos is expressed as a maximum.

Table 4-4: Diazinon and Chlorpyrifos Freshwater Load Allocations

	Diazinon (ng/L)			Chlorpyrifos (ng/L)		
	Interim (2002-2004)	Final (2005)		Interim (2002-2005)	Final (2006)	
Category	Maximum	Acute	Chronic	Maximum	Acute	Chronic
Wasteload Allocation	100	80	50	30	20	14
Load Allocation	100	80	50	30	20	14
TMDL	100	80	50	30	20	14

The final load allocations will come into effect when the EPA phaseout schedules for diazinon and chlorpyrifos are completed. The final diazinon load allocation is based on 4-day average of 50 ng/L, with a maximum 1-hour average concentration of 80 ng/L. The final chlorpyrifos load allocation is based on 4-day average of 20 ng/L, with a maximum 1-hour average concentration of 20 ng/L.

Chlorpyrifos in Upper Newport Bay

Table 4-5 presents interim and final TMDL allocations for chlorpyrifos in Upper Newport Bay. The interim allocation is equal to one-half the LC50 of *Mysidopsis bahia* (40 ng/L). *Mysidopsis bahia* was the most sensitive species in the CDFG data set that used to derive the acute and chronic recommended saltwater criteria for chlorpyrifos. The interim allocation is expressed as a maximum.

The final allocation is based on the CDFG recommended saltwater criteria for chlorpyrifos. Although the CDFG-derived acute concentration limit for chlorpyrifos is the same in both saltwater and freshwater (20 ng/L), the chronic limit in saltwater (9 ng/L) is less than the chronic limit in freshwater (14 ng/L).

The chlorpyrifos concentration in Upper Newport Bay is a function of the input concentration from the freshwater tributaries, and the degree of mixing between freshwater and saltwater. There will be sufficient mixing such that chlorpyrifos concentrations in Upper Newport Bay should be less than the concentration in the freshwater tributary channels. This was indeed the case during the sampling event conducted in Upper Newport Bay in January 1999. Thus, TMDL load and waste load allocations set at freshwater chronic criteria are expected to assure compliance with the saltwater numeric target.

Table 4-5: Chlorpyrifos Load Allocations
Upper Newport Bay (ng/L)

Category	Interim (2002-2005) Maximum	Final (2006) Acute	Chronic
Wasteload Allocation	20	20	9
Load Allocation	20	20	9
TMDL	20	20	9

Point Sources
The waste load allocation pertains to the point sources in the watershed that are NPDES and WDR permit holders. The permits will need to be revised to reflect the TMDL load allocation.

Non-Point Sources
The load allocation refers to the non-point sources in the watershed. Non-point sources are grouped into four categories:
- Agriculture
- Groundwater
- Atmospheric Deposition
- Sediment Remobilization

As discussed in the source analysis, except for agriculture, these sources are negligible contributors to the total load, and are not expected to contribute to pesticide-derived aquatic life toxicity.

Agricultural sources account for 2% to 12% of the diazinon load, and 12% to 15% of the chlorpyrifos load depending on the flow condition (**see Section 3.5**). The acute and chronic TMDL numeric targets will apply to discharges from agricultural land.

4.5 SEASONAL VARIATION

The climate of the Newport Bay watershed can be categorized into two seasons for water quality purposes: a dry season, and a wet season. Pesticide usage correlates roughly with the season, with increasing usage in the warmer months due to increased pest activity. However, runoff into the drainage channels is greatest during the wet season, and higher pesticide concentrations are observed during storm events. The higher pesticide concentrations account for the toxicity observed in stormwater samples collected in the watershed.

The chronic criterion is designed to ensure protection of aquatic life during all stages of life, including the most sensitive stages. As stated above, the concentration-based impairment requires that the TMDL apply during all seasons. There is no evidence of seasonal factors that increase or decrease toxicity, or render diazinon and chlorpyrifos more bioavailable or less bioavialable.

4.6 CRITICAL CONDITIONS

Because the TMDL is being expressed as a concentration, a detailed analysis of critical conditions is unnecessary. The same concentration limits will apply during all flow conditions and seasons.

During formulation of previous TMDLs, storm events greater than 50 cubic feet per second (cfs) were assumed to have enough momentum to convey the freshwater storm loads to the ocean in a short period of time. Thus these stormflows were not included in the load allocations. For the pesticide TMDL however, stormflow concentrations above the chronic or acute limits would cause unacceptable adverse impacts. Therefore the TMDL applies to the entire flow regime.

5.0 REFERENCES

Bailey, H.C., DiGiorgia, C., and Hinton, D.E., *Newport Bay Watershed Toxicity Study*, Submitted to the Santa Ana Regional Water Quality Control Board

California Department of Fish and Game (CDFG), 2000a. *Water Quality Criteria for Diazinon and Chlorpyrifos*

CDFG, October 2000. *Results of Chemical and Toxicological Analyses of Sediment and Chemical Analysis of Fish Tissue in Conjunction with the Red Imported Fire Ant Control Project*. Memorandum to SARWQCB

California Department of Pesticide Regulation (CDPR), July 1998. *Annual Pesticide Use Data; User Documentation*

California Department of Food and Agriculture (CDFA), March 1999. *Red Imported Fire Ant. California Action Plan*

CDPR, 1999-2000. *Preliminary Results of Pesticide Analysis and Acute Toxicity Testing of Monthly Surface Water Monitoring for the RIFA Project in Orange County.* (Monthly monitoring memos)

CDPR, 2000. *RIFA Insecticides and other Organophosphates: Use Pattern, Concentration, and Toxicity in Runoff Water, Source Identification, and Mitigation Measures*

Cooper, Ashli, 1996. *Diazinon in Urban Areas*. Prepared for the Palo Alto Regional Water Quality Control Plant

EXTOXNET, 1995-1996. Pesticide Information Profiles. (website: http://ace.orst.edu/info/extoxnet/pips/ghindex.html)

Lee, G. F., and S. Taylor, 1999. *Results of Aquatic Life Toxicity Studies Conducted During 1997-1999 in the Upper Newport Bay Watershed and Review of Existing Water Quality Characteristics of Upper Newport Bay and its Watershed*. USEPA 205(j) project report

Lee, G. F., and S. Taylor, 2001. *Results of Aquatic Toxicity Testing Conducted During 1999-2000 in the Upper Newport Bay Watersheds*. USEPA 319(h) project report

Giesy, J.P, et al, October 1998. *Ecological Risk Assessment of Chlorpyrifos in North American Aquatic Environments: Report of an Expert Panel*. Dow AgroSciences LLC Study ID: GH-C 4660

Hall, L. and R. Anderson, September 2000. *A Site-Specific Probabilistic Ecological Risk Assessment for Diazinon in California's Newport Bay Watershed*

Novartis Crop Protection Inc, 1997. *An Ecological Risk Assessment of Diazinon in the Sacramento and San Joaquin River Basins.* Technical Report 11-97

OCPFRD, 1999. *Orange County NPDES Stormwater Program, Annual Progress Report*

Santa Ana Regional Water Quality Control Board (SARWQCB), 1995. *Water Quality Control Plan [Basin Plan], Santa Ana River Basin – Region 8*

SARWQCB, 2001. *Final Problem Statement for the Total Maximum Daily Load for Toxic Substances in Newport Bay and San Diego Creek*

Scanlin, James and Arleen Feng, 1997. *Characterization of the Presence and Sources of Diazinon in the Castro Valley Creek Watershed*. Prepared for the Alameda Countywide Clean Water Program and the Alameda County Flood Control and Water Conservation District

Scanlin, James and Ashli Cooper, June 1997. O*utdoor Use Characterization of Diazinon and other Pesticides in Alameda County*. Prepared for the Alameda County Flood Control and Water Conservation District.

TDC Environmental, May 2001. Diazinon and Chlorpyrifos Products: Screening for Water Quality Implications.

USGS, 2000. *Stormflow Chemistry in the Santa Ana River below Prado Dam and at the Diversion Downstream from Imperial Highway, Southern California, 1995-98*.

USEPA, 1985. *Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses*, Office of Research and Development, Washington, D.C.

USEPA, May 1999. *Environmental Risk Assessment for Diazinon*.

USEPA, November 1999. *Pesticides Industry Sales and Usage*. 1996 and 1997 Market Estimates.

USEPA, June 2000. *Chlorpyrifos Revised Risk Assessment and Agreement with Registrants*.

USEPA, August 2000a. *Letter from Alexis Strauss to the Central Valley Regional Water Quality Control Board*.

USEPA, August 2000b. *Ambient Aquatic Life Water Quality Criteria: Diazinon (Draft)*.

USEPA, January 2001. *Diazinon Revised Risk Assessment and Agreement with Registrants*.

Wilen, Cheryl 2001. *Residential Pesticide Use and Attitude Survey, San Diego Creek Watershed* (forthcoming)

California Regional Water Quality Control Board
Santa Ana Region

September 26, 2001

ITEM: 16

SUBJECT: Toxics Total Maximum Daily Loads (TMDLs) for the San Diego Creek/Newport Bay Watershed

Discussion

Pursuant to the requirements of Section 303(d) of the Clean Water Act, the Regional Board listed Newport Bay and San Diego Creek as impaired due to toxic substances. The 303(d) listing triggered the requirement that TMDLs be developed for those toxics causing impairment. Regional Board and US Environmental Protection Agency (USEPA) staff are coordinating efforts to develop these TMDLs. USEPA is required by a consent decree to complete toxics TMDLs in Upper and Lower Newport Bay and San Diego Creek by April 15, 2002.

The 303(d) listing was general, identifying pesticides, metals, priority organics, and unknown toxicity as the sources of impairment. Consequently, the first step in the TMDL process was the analysis of available data to identify the specific constituents of concern. Board staff reviewed available data on water column chemistry, sediment chemistry, fish and shellfish tissue concentrations (reflecting bioaccumulation), and toxicity. These data were compared to appropriate criteria and guidelines to determine what substances appeared to be causing violations of the narrative and numeric toxics objectives specified in the Basin Plan. The data reviewed and the results of the evaluation are described in the Problem Statement for the Total Maximum Daily Load (TMDL) For Toxic Substances in Newport Bay and San Diego Creek. This report was presented to the Regional Board at the January 19, 2001 Board meeting.

More recently, the USEPA conducted an independent analysis of the data, emphasizing the last five years of water quality, sediment, and fish tissue data, to identify the chemicals USEPA believes cause impairment. USEPA also reviewed new data and updates to existing data sets that became available after the completion of Board staff's Problem Statement. USEPA has formulated a list of toxicants for which TMDLs will be developed. USEPA's list is in general agreement with the Regional Board's toxics TMDL list.

The development of the TMDLs is a cooperative effort between the USEPA and Regional Board staff. To assure that the consent decree deadline of April 15, 2002 is met, the approach being employed to develop the toxics TMDLs differs from that used for the prior Newport TMDLs. For the prior TMDLs, the requisite components, including source analysis, numeric target(s), wasteload and load allocations, and total maximum daily load (the so-called "technical TMDL"), were developed together with an implementation plan and schedules. The technical TMDL and implementation plan were presented to and adopted by the Regional Board as a Basin Plan amendment (BPA). For the toxics TMDLs, however, there is not sufficient time to complete the implementation plan and Basin Plan Amendment process by April 15, 2002. Therefore, Board staff and USEPA are developing technical TMDLs that will be promulgated by USEPA on or before April 15, 2002. Board staff will subsequently prepare implementation plans and Basin Plan Amendment packages for consideration by the Regional Board.

Board staff are working on the TMDLs for diazinon, chlorpyrifos, and selenium, while USEPA will complete the technical TMDLs for the other toxicants. A letter from David Smith (attached), USEPA TMDL Team Leader, describes the process by which USEPA will combine the Regional Board and USEPA staff reports into two separate documents: a toxics TMDL (for all toxicants) and the technical support documents. It is expected that the documents will be available for comment by January 2002. USEPA will then proceed with toxics TMDL promulgation by April 15, 2002.

Once the TMDLs are promulgated, Regional Board staff will develop implementation plans and Basin Plan amendments for the TMDLs to be incorporated into the Basin Plan. A copy of the draft diazinon and chlorpyrifos TMDLs is attached for your review. Substantial work has also been accomplished on the selenium TMDL. Board staff expects to present an overview of both TMDLs to the Regional Board at the September 26 Board meeting.

Attachments:

9/7/01 Letter from David Smith, US EPA
Draft Diazinon and Chlorpyrifos TMDLs

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105-3901

September 7, 2001

Mr. Gerard J. Thibeault
Executive Officer
Santa Ana Regional Water Quality Control Board
3737 Main Street, Suite 500
Riverside, CA 92501

Dear Mr. Thibeault,

The U.S. Environmental Protection Agency (EPA) continues to develop TMDLs for toxic substances in Newport Bay and San Diego Creek. I write to provide a progress report and to introduce Peter Kozelka, EPA Region 9 Water Division. Dr. Kozelka is our designated TMDL liaison to the Santa Ana Regional Board, and he has been actively involved with this project.

As you know, the scope of these TMDLs is to address water quality impairment due to a group of "toxic" chemicals, more specifically PCBs, metals and pesticides. Potential water bodies include: Santa Ana/Delhi Channel, San Diego Creek and its freshwater tributaries, Upper and Lower Newport Bay, and Rhine Channel. Whereas we view these TMDLs as a cooperative effort between EPA and Regional Board staff—and we greatly appreciate your staff's commitment to support TMDL development—let me reiterate that EPA (alone) is under consent decree to complete toxics TMDLs by April 15, 2002.

In December 2000, Ken Theisen, Regional Board staff, provided a "problem statement" describing which chemicals were probable cause of impairment with respect to each waterbody. EPA staff has completed an independent assessment of water column, sediment and fish tissue monitoring data (emphasis on last five years) to identify the chemicals we believe cause impairment. For our assessment, we included several new data sets and updated results for existing data sets, and EPA's assessment shows fairly good agreement with chemicals identified by RWQCB staff as to chemicals of primary concern.

We will approach these TMDLs as follows:

Regional Board staff will develop TMDLs for Chlorpyrifos, Diazinon and Selenium.

EPA Region 9 staff will develop TMDLs for organochlorine compounds (including legacy pesticides such as DDT) and metals. Some toxicants will be addressed for all water bodies, whereas others will address impairment within specific water bodies. For example, we may write TMDLs for certain toxicant(s) in San Diego Creek only, or we may write TMDLs for toxicant(s) in Rhine Channel as a water body separate from Lower Newport Bay.

We anticipate combining all staff reports into two documents: the toxics TMDL (for all toxicants) and the technical support documents (with additional scientific details regarding source analysis per toxicant, modeling results and other relevant information). These documents will be available for public comment in January 2002. Notification will likely include addressees of Santa Ana RWQCB Basin Plan and Newport Bay Watershed Management Committee mailing lists, as well as public announcement. We expect a 30 to 60 day comment period. To ensure our commitment to Toxics TMDL consent decree, EPA will establish these TMDLs by April 15, 2002.

Sincerely,

David Smith
TMDL Team Leader